

# METALLURGIA

*The British Journal of Metals*

(INCORPORATING THE METALLURGICAL ENGINEER)

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## PRINCIPAL CONTENTS IN THIS ISSUE:

	Page		Page
Plan the Re-establishment of Trade and Industry .....	51-52	A Review of Basic Open-Hearth Practice at an Australian Plant. By R. L. Knight .....	77-80
Magnesium from Canadian Dolomite .....	52	<i>In this, the concluding, part of this review attention is directed to slag control in the production of semi-killed steels, phosphorised sheet bar, rimming steel, and alloy and forging steels.</i>	
A Professional Institute Medal Award.			
Ternary Cadmium Alloys and Ternary Alloys Containing Cadmium. By O. P. Einerl, D.Eng., M. Inst. M. ....	53-61	Chromium-Manganese Stainless Irons .....	84-85
<i>A considerable amount of information on cadmium and cadmium-containing alloys is given in this survey which includes some of their practical applications. A useful bibliography is also given.</i>		<i>An investigation in the iron chromium-manganese alloys is described, and their engineering properties and corrosion resistance considered.</i>	
Thermodynamic Considerations in the Corrosion of Metals. By Prof. J. C. Warner .....	61-66	Silicon-Bronze Castings .....	85-86
<i>Available thermodynamic data are reviewed and used to calculate the spontaneity of corrosion reactions for most of the common metals in deaerated water, and in water saturated with carbon dioxide and in free air. The results of each calculation are summarised.</i>		<i>Some theoretical aspects connected with the production of serviceable castings are discussed.</i>	
National Fuel Economy .....	66	Directional Characteristics of Single-Texture Copper Strip. By M. Cook, D.Sc., and T. Ll. Richards, B.Sc. ....	87-89
New Laboratories of the British Cast-Iron Research Association .....	67-70	<i>The resolved shear on the slip planes in slip directions has been calculated in terms of the applied stress for copper strip with the single-texture type of structure. These values have been correlated with tensile strength and elongation values.</i>	
The Mineral Monazite. By L. Sanderson .....	71-72	Machining Magnesium Alloys .....	90
<i>Some data concerning the elements thorium and cerium are given, and their extraction from monazite is briefly described.</i>		<i>An antiseptic coolant which improves finish and reduces fire risk.</i>	
The Gas-cutting Process and Its Effects on Steel. By T. J. Palmer .....	73-76	The Desirability of Removing Sulphur from Gaseous Fuels for Heating Ferrous Metals. By A. Preece, M.Sc. ....	91-93
<i>General requirements are discussed and attention directed to some metallurgical aspects. It is shown that the process has no detrimental effect on the usual range of mild steels. The metal adjacent to the cut edge shows a change in structure with a slight carbon increase.</i>		<i>The results obtained in a general study of the high-temperature oxidation of steels are considered with special reference to the harmful effects of the sulphur content of the furnace atmosphere.</i>	
Tropenas Converter Practice. By E. C. Pigott .....	81-83	Thickness Testing of Electrodeposits .....	94
<i>The development of this converter is briefly reviewed and an account of its operation is given. The need of scientific control to obtain the best results is emphasised.</i>		The Conservation of Nickel in Electrical Resistance Alloys .....	95-98
		<i>Alternative material for control resistances are described.</i>	

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## Plan to Re-establish Trade and Industry

**M**ANY people in this country seem to be under the impression that the worst of the war is over and that victory is almost at hand. There is no doubt that the turn in the fortunes of war has greatly encouraged the nation and brought about increased optimism for the future, but it is only necessary to keep in mind the countries that have been and are being ravaged by the enemy to realise that much requires to be done before victory will be achieved. The task before the Allied nations remains a stupendous one, certainly it is not one which can be regarded lightly. Momentous decisions have been taken at Washington and at Algiers, one of the objects of which will be to intensify the war; indeed, we have Mr. Churchill's assurance that amphibious operations of peculiar complexity and hazard on a large scale are approaching.

While discussions at Washington have apparently been mainly concerned with the conduct of the war, some attention has been given to the formation of machinery to prepare plans for peace. A notable example of this is the proposal to set up a United Nations Relief and Rehabilitation Administration, a draft agreement on which has been circulated to all the United Nations for their consideration. Doubtless, this subject formed part of the discussions and the draft agreement will embrace the views of representatives of this country as well as of the United States.

The agreement is based upon the belief that provision for relief and rehabilitation in war-devastated countries must be a joint effort of all the United Nations who will contribute to that effort on the principle: From each according to his capacity, to each according to his need. It suggests that all the Governments of the United Nations, or associated authorities, who become signatories to the agreement shall be members of the Administration, with the right to appoint one representative to its Council, which will be its policy-making body. But for practical purposes a much smaller committee, to be known as the Central Committee of the Council, will do most of the day-to-day work of policy direction.

Under the agreement each member Government must pledge its full support to the Administration within the limits of its available resources and subject to the requirements of its constitutional procedure, through contributions of funds, materials, equipment, supplies and services. In other words, each of the United Nations, according to its capacity, must contribute to the common pool, from which the Administration will draw to relieve the war-torn countries according to

their needs. The spirit behind this plan is excellent, and it is hoped that the proposals will prove acceptable, so that the Administration might be brought into being without delay to set about its vital work. Such a plan will be necessary to enable the stricken countries to have breathing space in which to re-establish themselves, but it should be regarded as complementary to a world plan for the establishment of international trade relations after the war. Carried out in the same spirit, and primarily with a view to being of service to mankind in general, an industrial plan which would provide a framework within which the various countries could develop their trade and industry would reduce chaos after the war. Indeed, as with the proposed relief Administration, it could be prepared to function as a nation becomes freed from the Nazi yoke. Thus, problems of industry could be tackled immediately the problems of famine, want, pestilence and destruction have been, at least, partially overcome.

Since this country will be one of the countries largely responsible for the relief of other countries, it will be necessary for industry to effect changes from war to peace-time requirements as quickly as possible, and in order that these changes will be made on a sound basis, there should be no delay in planning for the future. It is appreciated, of course, that without victory there can be no free, ordered, peaceful life for peoples or individuals, and that victory can only be achieved if we reduce the necessities of life to a minimum and give priority to war production and fighting power. But it is also appreciated that the moment the fighting power of the enemy collapses, this country will be faced with every possible major political, economic and social problem, and we shall have to find a reasonably adequate solution for all these problems if we do not wish to lose the peace, after having won the war.

Many of us remember what happened after the last war, and while it is not likely that the mistake of disarmament will be repeated, it is not difficult to imagine the vast changes in production and man-power which will accompany the cessation of hostilities. Problems of destruction and disorganisation will be on an infinitely larger scale than in 1919. Destruction from the air and by subsequent advances and retreats of great armies over long distances have been and will continue on a tremendous scale. The occupied countries are disorganised, weakened by constant undernourishment, and in some cases depopulated by the deportation of hundreds of thousands of their nationals and the murder of thousands more.

We shall have to work and work hard to do our part in helping to restore these countries, but if, as many people seem to imagine, the end of the war may be soon, as a result of the collapse of the Axis powers, no time should be lost

The fact that goods made of raw materials in short supply owing to war conditions are advertised in "Metallurgia" should not be taken as an indication that they are necessarily available for export.

in formulating a plan acceptable to the United Nations and which can be put into operation at short notice. For this purpose some form of international agreement must be reached and international machinery devised to control international trade, at least during the reconstruction period. There are many objections to any agreement of this character, which may be easy to draw up, but extremely difficult to put into execution. It will mean the continuance of rationing, and the problems associated with priority of supplies, involving difficulties of agreement, of finding common denominators and sequences of urgency, and the possibilities of delay and frustration. But the evil of a free-for-all fight for goods and markets should be guarded against as contrary to the common good. Some form of international agreement may enable us to find solutions that will avoid many of the disadvantages which at present seem unavoidable. Just as victory can only be achieved by common effort, so common effort is needed in the reconstruction period and in the re-establishment of trade and industry.

## Magnesium from Canadian Dolomite

### A Professional Institute Medal Award

THOSE who have followed developments in Canada associated with the reduction of calcined dolomite with ferro-silicon will be interested to learn that Dr. L. M. Pidgeon, who carried out the research work on Canadian dolomite in the laboratories of the National Research Council, has been awarded a Professional Institute Medal for 1943 for his outstanding scientific contribution to Canada's war effort by developing a process for the extraction of magnesium from dolomite deposits.

Owing to wartime restrictions and other causes, full details of the process cannot be revealed. The abundance of dolomite in nearly all countries of the world has caused widespread interest to be taken in its reduction with ferro-silicon to produce magnesium. The main steps in the process are very similar to those in the carbide reduction method. Dolomite is calcined, pulverized, and mixed with ferro-silicon that has been ground to a suitable fineness. The mixture is briquetted and charged either to externally heated retorts operated under a vacuum or to furnaces through which inert gas is circulated. The magnesium vapour is condensed on the sides of a water-cooled condenser and removed as a ring of pure, solid metal. During the reduction process, the silicon combines with the calcium oxide to form dicalcium silicate, which does not melt at the temperatures involved, and the spent briquettes, consisting mostly of dicalcium silicate, are removed in the same shape as they were charged. In this process, relatively low temperatures are required, and the magnesium is obtained in solid form direct from the raw material. Furthermore, because of the low temperatures involved, a very pure metal is obtained as few of the impurities are volatilised with the magnesium.

The process developed by Dr. Pidgeon is of outstanding value on account of the low capital cost of the installations required, and of the speed with which the plants can be constructed or expanded. The technological importance of his work is indicated by the fact that six plants, having a total value of \$40,000,000 and with an

estimated daily aggregate output of 135 tons, are already in operation or in an advanced stage of construction in Canada and the United States.

Born in 1903, Dr. Pidgeon obtained his B.A. degree at the University of Manitoba in 1925, winning the Gold Medal in Science. From McGill University he secured his M.Sc. degree in 1927, and his Ph.D. in 1929. He continued his studies at Oxford University under a Sir William Ramsay Memorial Fellow for Canada scholarship (research under A. C. Agerton, F.R.S., Clarendon Laboratory, Oxford), where he obtained his B.Sc. in 1931. On his return to Canada, he joined the staff of the National Research Council, where, in 1937, he was put in charge of magnesium research work.

After giving considerable time to the study of established methods of producing magnesium, Dr. Pidgeon concentrated investigations on direct reduction processes. The advantages of such a process had long been appreciated, and many workers had given it careful study before finally dismissing it as impossible of accomplishment in practice. Fortunately, this did not deter Dr. Pidgeon in his efforts to develop a process. It was found that by far the most effective reaction was between silicon and calcined dolomite. A small experimental apparatus was set up, and it was discovered that the reaction would take place at a much lower temperature than had been expected.

Numerous practical difficulties had to be overcome, especially in designing apparatus capable of carrying out the laboratory process on a large scale. Experimental work was carried out in a 4-in. retort and then in a pilot plant with 8-in. retorts and a general system of operation developed somewhat analogous to the horizontal zinc practice.

As previously mentioned, the process developed by Dr. Pidgeon consists of briquetting ground ferro-silicon with dead-burnt dolomite and heating these briquettes in a steel retort fitted with a condenser, to a temperature of about 1,150° C. Air is pumped out of the retort and condenser, and, as the reaction proceeds, metallic magnesium of 99.98% purity is deposited on the removable lining of the condenser. The cycle of operations lasts about six hours. Differential contraction of the steel and magnesium brings about separation of the two metals, and the magnesium "pipe" can be transferred directly to the foundry without further purification or treatment. This magnesium "pipe" is a solid dense crystalline mass, which is subsequently melted down under flux into ingots, or added direct to molten aluminium for the production of aluminium-magnesium alloys. In this process the reaction proceeds smoothly without difficulty or danger, and when the retorts are opened the magnesium is in solid massive form, precluding the possibility of explosion or fire.

## Vickers-Armstrongs Limited Board

VICKERS-ARMSTRONGS, LTD., intimate the appointment to their Board of Mr. Hubert Thompson and Mr. J. M. Ormston, M.B.E.

Mr. Thompson, who for some years has been commercial manager at the Barrow Works, has been appointed deputy to Sir James Callender, the general manager of these works, whilst Mr. Ormston, the shipbuilding manager at Barrow, has been appointed general manager at the Naval Yard, Walker-on-Tyne.

# Ternary Cadmium Alloys and Ternary Alloys Containing Cadmium

## A Survey of their Practical Application

By Dr. O. P. Einerl, M.Inst.M.

*A considerable amount of information is available concerning cadmium and the cadmium-containing alloys, but results of recent investigations have not associated their practical applications. In this survey the author directs particular attention to the ternary cadmium-containing alloys. Although comprehensive it is not exhaustive, but references to more specialised treatises, and to original papers, are made for those wishing to study particular points.*

THE increasing importance of cadmium can be appreciated from the fact that the production of cadmium on a commercial scale, which began between 1904 and 1906 in the United States and in Germany, had reached only 90 tons in 1920, but in 1937 had risen to 2,000 tons, in 1939 to 4,000 tons, half of it produced in United States plants, which since have largely increased their output.<sup>1</sup> American production in 1941 was 3,800 tons, which is 60% of a world production of about 6,300 tons.

Five groups of ternary cadmium alloys have gained technical importance:—

- (A) The cadmium alloys with aluminium and a third component.
- (B) The cadmium alloys with copper and a third component.
- (C) The cadmium alloys with tin and a third component.
- (D) The cadmium alloys with antimony and a third component.
- (E) The cadmium alloys with bismuth and a third component.

### Group A.—Cadmium Alloys with Al-Mg, Al-Zn, Al-Sn and Al-Cu

(1) *The System Cd-Al-Mg.*—This ternary system is based on the following binary systems:—

(i) The system aluminium-cadmium, established by Gwyer<sup>2</sup> and Hanson and Blumenthal<sup>3</sup>, which is characterised by the fact that these two metals are immiscible in the liquid state, and that melts of aluminium with more than 10% Cd separate into two layers when they solidify.

(ii) The system aluminium-magnesium, established by Dix and Keller<sup>4</sup> and by Hume-Rothery<sup>5</sup>, has been described with the compounds  $\text{Al}_3\text{Mg}_2$  and  $\text{Al}_2\text{Mg}_3$ .

(iii) The system cadmium-magnesium, which is very complicated, and the latest investigations have been made by Hume-Rothery and Raynor.<sup>6</sup>

The ternary phase diagram, according to Jänecke<sup>7</sup>, is shown in Fig. 1. It can be seen that the addition of magnesium considerably reduces the field of immiscibility in the liquid state of the system cadmium-aluminium.

As the overwhelming majority of technically applied ternary alloys is based on ratios between the three components in which one of them is predominant (corresponding to the three corners of the phase diagram triangle), it will be sufficient to deal with the alloys in the "corner" only—i.e., the "aluminium corner" of a ternary alloy, which means that aluminium is predominant in the alloys discussed.

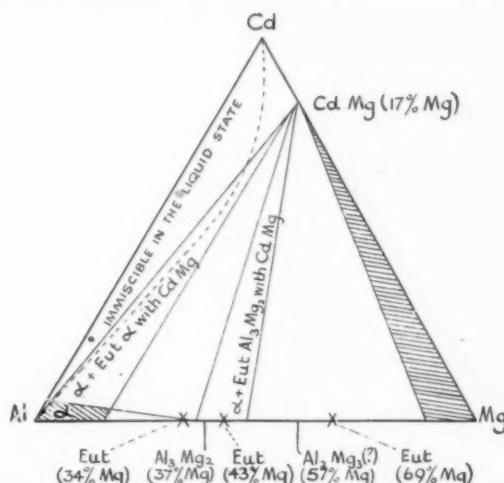


Fig. 1.—The Cd-Al-Mg phase diagram.

(a) The aluminium corner of the system Cd-Al-Mg. In the triangle marked with alpha there is a solid solution of magnesium and cadmium in aluminium. Situated in this field are the aluminium alloys, covered by a German patent of the Aluminium Works, Neuhausen,<sup>8</sup> which have also a small addition of manganese; furthermore, the French alloy Inalium (Comp. des alliages de l'aluminium, Asnières) with 1·7% Cd and 1·2% Mg, besides 0·5% Si, which has, as a wrought alloy, a tensile strength of 11–13 tons per sq. in., 18–22% elongation, and 50 to 60 Brinell hardness.

Alloys from this field can also be advantageously used as hard solders for Mg-containing aluminium alloys of the type MG 5 and MG 7 (as manufactured by J. Booth and Co., Ltd., Birmingham).

A recent patent by W. Mills<sup>9</sup> claims an alloy suitable

<sup>1</sup> Yearbook of the Am. Bureau of Metal Statistics, 23rd issue, 1942.

<sup>2</sup> Z. anorg. Ch., 1908, **57**, p. 149.

<sup>3</sup> Metallurkisch., 1931, **10**, 925, and 1932, **11**, 671.

<sup>4</sup> Trans. Am. Inst. Min. Met., 1929, 351.

<sup>5</sup> J. Inst. Metals, 1938, **63**, p. 201.

<sup>6</sup> Proc. Roy. Soc., 1940, **174**, p. 471.

<sup>7</sup> Z. Metallk., 1938, **30**, 427.

<sup>8</sup> German Patent 605,405 of 1930.

<sup>9</sup> Brit. Pat. 550,516 of 1941.

for aluminium bearings with 5% Mg, 10% Cd, balance aluminium with an addition of 0.5% Cu.

(b) The magnesium corner. In the triangle which extends from pure magnesium to the compound Cd-Mg, and to an aluminium content of up to 10% Al, are alloys which contain a solid solution of aluminium and cadmium in magnesium.

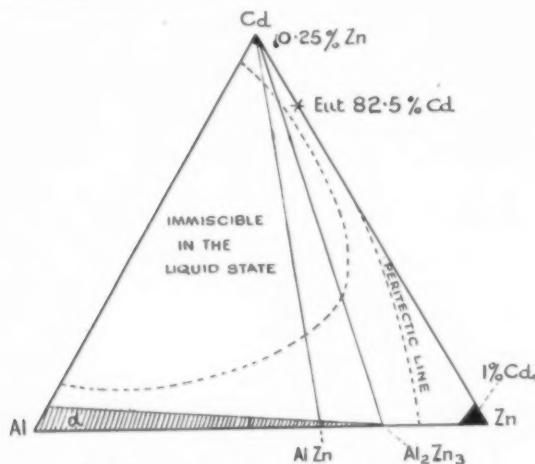


Fig. 2.—The Cd-Al-Zn phase diagram.

The American magnesium alloy, Downmetal A (Alloy 13), which is being used for pistons, has an addition of up to 0.3% Cd besides 8.3-9.7% Al, balance magnesium (tensile strength 14-16 tons per sq. in., 9-12% elongation, 50 Brinell).

The electron alloy AZD for sheets<sup>10</sup> contains 5% Al, 3% Cd, besides 3% Zn and 89% Mg. The alloy is used for highly stressed parts, and shows the following figures:—Soft : 19-21 tons, 10-12% elongation, 60 Brinell; hard : 22-26 tons, 1-3% elongation, 70 Brinell.

Also the magnesium alloys with Al addition and contents of 10% Cd and more have been tried. It can be said that all the alloys in the magnesium corner show good mechanical qualities, and further development is possible in this region.

When the Cd content, as well as the Al content, is considerably raised one will find, approximately in the centre of the phase-diagram Cd-Al-Mg a ternary eutectic with a melting point of only 395° C., an alloy which can be used as a soft solder for aluminium alloys. The soft solders near the eutectic belong to the field in the middle of the phase diagram, and the micrographs are showing accordingly solid solution alpha and eutectic of Al<sub>2</sub>Mg<sub>3</sub> with CdMg.

(c) The cadmium corner is up to now without practical importance.

(2) *The System Cd-Al-Zn (Phase diagram Fig. 2).*—Addition of zinc reduces in the same way as the addition of magnesium (see note after Fig. 1) the field of immiscibility of the system Al-Cd in the liquid state.

(a) The aluminium corner of the system Cd-Al-Zn. In the triangle marked with alpha, which extends from pure aluminium to the compound Al<sub>2</sub>Zn<sub>3</sub>, and to a cadmium content rising to 4% Cd, there is a large field of solid solution of Cd and Zn in Al. An early German

patent<sup>11</sup> claimed alloys from this field up to 20% Zn and up to 5% Cd, and stated that these alloys could be age-hardened. The photomicrograph, Fig. 3, shows such an alloy with 3.4% Cd and 10% Zn, balance aluminium. Micrographs of alloys with up to 2% Cd and 10% Zn, balance aluminium, have been published

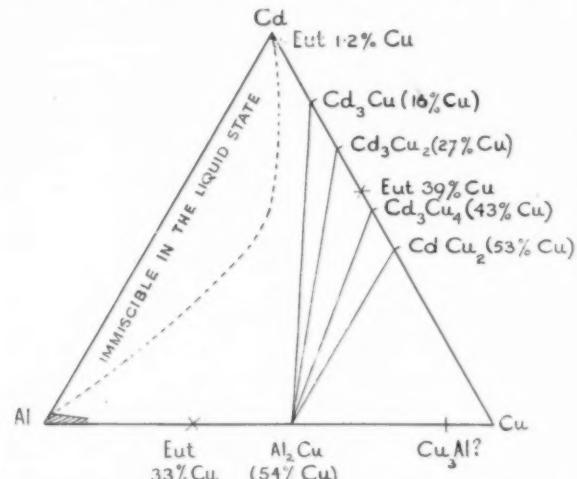


Fig. 4.—Approximate phase diagram for the system, Cd-Al-Cu.

by Budgen.<sup>12</sup> Further developments might be possible here.<sup>13</sup>

(b) The zinc corner. Cadmium (up to 1% Cd) forms a solid solution in zinc. This limit of solid solution is very likely also the reason why the Cd content in zinc ores is limited to this figure. The hardness of commercial zinc is dependent largely on its Cd content, which renders zinc hard and, to some extent, brittle. Cadmium containing zinc is unsuitable for making galvanised wire, as the coating would peel off. Small additions of aluminium can remove this difficulty by forming an alloy in the small black field in the zinc corner of the above phase diagram, Fig. 2.

Alloys with higher contents, e.g., 75% Zn, 20% Cd and 5% Al, were tested and recommended as aluminium solders.<sup>14</sup>

(c) Between pure zinc and the eutectic alloy with 82.5% Cd there is an alloy suitable as solder for end connections of steel cables with about 70% Cd, 30% Zn and traces of Al, similar to the composition of the solder DTD 221 with 70.5-71.5% Cd, 0.06% Sb, balance Zn, and with a melting point of only 263° C. (Cazin solder).

(3) *The System Cd-Al-Sn.*—Early investigations have been made by Wright<sup>15</sup>, but this system is up to now only of little practical importance.

An alloy with 74% Al, 22% Cd and 4% Sn is mentioned in American patent 1,121,269, and an alloy for use in welding with 90% Al, 5% Cd, 2.5% Sn and 2.5% Bi is covered by a British patent.<sup>16</sup>

(4) *The System Cd-Al-Cu (Phase diagram Fig. 4).*—No constitutional diagram has been published. The addition of copper reduces in the same way as the

<sup>11</sup> German Patent 272,492 of 1915.

<sup>12</sup> J. Chem. Soc., 1924, **125**, 1,642.

<sup>13</sup> Ann. Spanish Soc. for Phys. Chem., 1935, **33**, 10.

<sup>14</sup> Am. Welding Soc. Journal, Aug., 1937, p. 37.

<sup>15</sup> Proc. Roy. Soc., 1894, **55**, 131.

<sup>16</sup> Brit. Patent 243,156 of 1929.

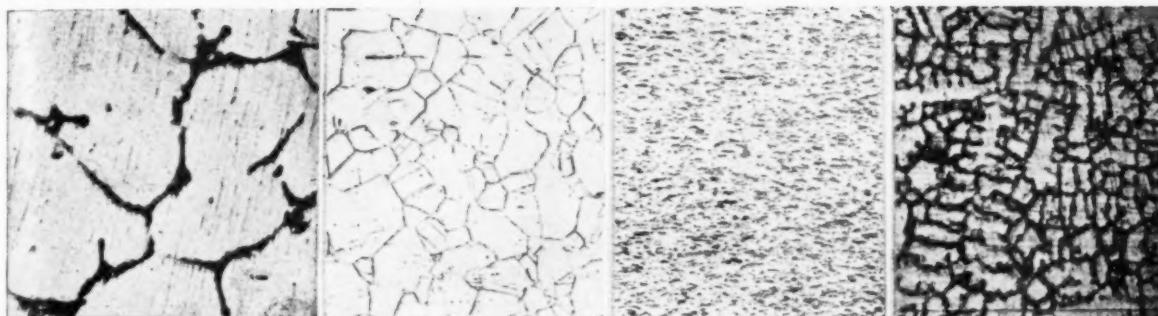


Fig. 3.—Cd-Zn-Al alloy, German patent 272,492 (10% zinc, 3.4% cadmium, balance aluminium). Etched NaOH.  $\times 30$ .

Fig. 6.—Cadmium-copper trolley wire as drawn.  $\times 100$ .

Fig. 7.—Cadmium-copper trolley wire after annealing for 30 mins. at  $680^{\circ}\text{C}$ .  $\times 100$ .

Courtesy of Bolton and Sons (Widnes).  
Fig. 8.—Hard-bronze welding electrode, 94.2% Cu, 5.7% Cd, 0.1% Mg.  $\times 100$ .

addition of Mg or Zn the field of immiscibility of the system Al-Cd in the liquid state, and the phase diagram will therefore be approximately as indicated in Fig. 4.

(a) The aluminium corner. There is a very small field of solid solution of cadmium and copper in aluminium, which is being claimed for aluminium alloys by a French patent<sup>17</sup> (with 4–6% Cu, 2–4% Cd, balance aluminium) and by two British patents<sup>18</sup> (with 6–8% Cu, up to 1.5% Cd, and small amounts of Ni and Mg) for engine pistons, cylinder heads and other castings to possess good mechanical strength at high temperatures.

As a commercial alloy for diecastings and sheets the French alloy Aeral<sup>19</sup>, with 1–2% Cd, 4–5% Cu and small amounts of Mg, has been developed. Higher magnesium additions (up to 1%) lead to the cadmium-containing Dural alloys, e.g., the Italian Adriatico D<sup>20</sup>, or to the British specification DTD 294, with 2–4.5% Cu, 0.5–2.5% Cd, besides 0.2–1.5% Mg and up to 0.5% Mn, which is suitable for solution treatment (castings not pistons), and has a tensile strength of 14–17 tons and 3–5% elongation. (Aeral A of International Alloys, Ltd.)

Cadmium is further present in the German pressure die-casting alloys of the specification DIN 1744, besides 6–8% Cu and 1.5–2% Si, balance aluminium, where it reduces the tendency to the formation of cracks.

Outside the field of solid solution in the aluminium corner lies the silver-containing aluminium alloy "MacAdams Argental," with 12% Cu, 5% Cd, 1% Ag and 82% Al.

A recent patent by W. Mills<sup>21</sup> claims an aluminium alloy with increased resistance to corrosion, improvement in machinability, and in bearing properties, containing 1–6% Cu, 0.5–3% Ni, 0.5–2% Cd, balance aluminium, with additions of 0.5–0.75% Mg.

(b) The copper corner. Nothing has been published on the influence of aluminium additions to cadmium-copper alloys for overhead lines, or on the influence of cadmium in cast or wrought-aluminium bronze with 9–10% aluminium.

(c) The cadmium corner. Cadmium retains only 0.07% Cu in solid solution, and there is a eutectic alloy with 1.2% Cu and a melting point of  $314^{\circ}\text{C}$ . between pure Cd and the intermetallic compound  $\text{Cd}_3\text{Cu}$ .

Alloys of this kind, and with an addition of up to 0.5% Al, have been tried as bearing metals, but their mechanical properties are not by any means as good as those with an addition of Mg (DTD 217), which will be dealt with later on.

#### Group B.—Cadmium Alloys with Cu-Mg, Cu-Ag and Cu-Ni.

(1) *The System Cd-Cu-Mg (Phase diagram Fig. 5).*—This system is based on the following binary systems, which are fully established:

(i) The binary system Cu-Cd, investigated by Jenkins and Hanson,<sup>22</sup> contains the intermetallic compounds  $\text{Cd}-\text{Cu}_2$  (with 53% Cu),  $\text{Cd}_3\text{Cu}_4$  (43% Cu),  $\text{Cd}_3\text{Cu}_2$  (27% Cu) and  $\text{Cd}_3\text{Cu}$  (16% Cu). One eutectic exists between the compounds  $\text{Cd}_3\text{Cu}_4$  and  $\text{Cd}_3\text{Cu}_2$  with a

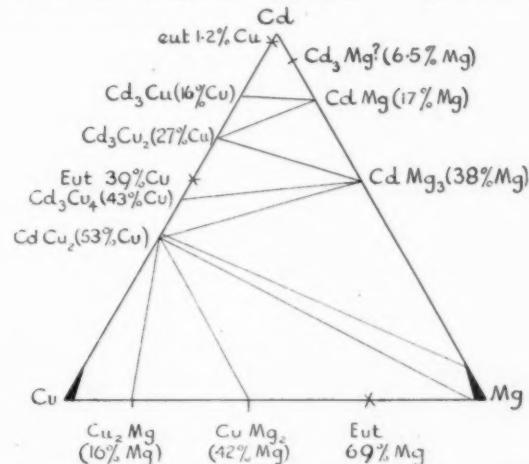


Fig. 5.—The Cd-Cu-Mg phase diagram (approximately).

melting point of  $544^{\circ}\text{C}$ : (39% Cu), and another one with 1.2% Cu and a melting point of only  $314^{\circ}\text{C}$ . between pure Cd and the compound  $\text{Cd}_3\text{Cu}$ .

(ii) The binary system Cd-Mg has been established by Hume-Rothery and Raynor,<sup>23</sup> and contains the compounds  $\text{Cd}_3\text{Mg}$  with 6.5% Mg,  $\text{CdMg}$  with 17% Mg, and  $\text{CdMg}_3$  with 38% Mg.

(iii) The system Cu-Mg was first established by

<sup>17</sup> F.P. 333,437.

<sup>18</sup> Brit. Pat. 172,155 and Brit. Pat. 550,516 of 1941. (W. Mills.)

<sup>19</sup> Comp. des alliages de l'aluminium, Asnières, France.

<sup>20</sup> Alfa Romeo, Milan, Italy.

<sup>21</sup> Brit. Pat. 550,738 of 1941.

<sup>22</sup> J. Inst. Metals, 1924, **31**, p. 257 and 1925, **34**, p. 103.

<sup>23</sup> Proc. Roy. Soc., 1940, **174**, p. 471–486.

<sup>24</sup> Z. anorg. Ch., 1908, **57**, 31.

Sahmen,<sup>24</sup> and more recent investigations have been published by Jones.<sup>25</sup> It contains the intermetallic compounds  $\text{Cu}_2\text{Mg}$  with 16% Mg and  $\text{CuMg}_2$  with 42% Mg. There is a eutectic with 69.3% Mg and a melting point of 485°C. between pure Mg and the compound  $\text{CuMg}_2$ .

The ternary phase diagram has not yet been published, it will be approximately as shown in Fig. 5.

(a) The copper corner. Copper containing 0.8–1% Cd and very small amounts of Mg or Li has excellent electrical and mechanical properties for trolley wires and other electrical purposes.<sup>26</sup>

A British patent of the Westinghouse Electric Co.<sup>27</sup> uses a Cd-Cu alloy with 0.5–1% Cd for the tip of the finger which exerts pressure on the brush of the dynamo machines.

The British specification DTD 208 calls for a cadmium content of 0.8–1.2% Cd for wires and strips with minimum 25 tons proof stress and 25 tensile strength.

Although the electric conductivity of copper is reduced by 10% by adding cadmium, the tensile strength is increased by over 50%. Moreover, the temperature at which cold-drawn copper begins to lose its acquired hardness is raised considerably by the presence of Cd.

The British Standard Specifications No. 23, No. 175 and No. 672 deal with wrought copper alloys, with 99% Cu and 0.4–1% Cd, in the discretion of the manufacturer.

BSS 23, for trolley wire, does not specify the composition, but calls for a minimum conductivity of 92% of the value for hard-drawn copper. The tensile strength

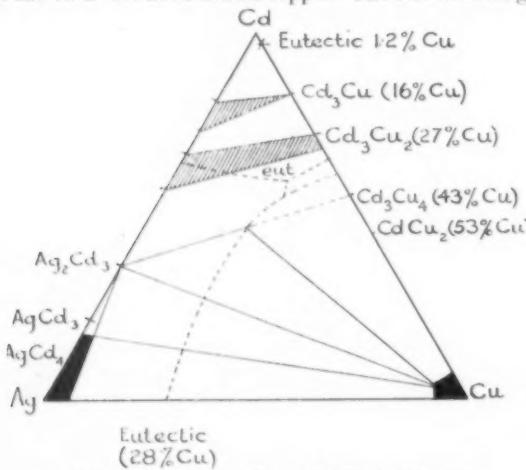


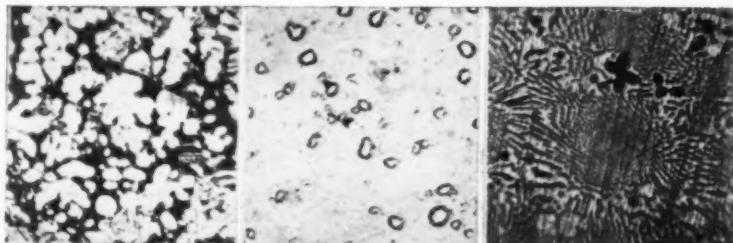
Fig. 11.—The Cd-Cu-Ag phase diagram.

of cadmium-containing contact wire reaches 30 tons, and it is possible to raise it to 34 tons, in which case the conductivity goes down to only 88% of the standard for hard-drawn wire. The photomicrographs (by courtesy of Bolton and Sons, Widnes) show cadmium-copper trolley wire as drawn (Fig. 6), and after annealing for half-hour at 680°C. (Fig. 7).

25 *J. Inst. Metals*, 1931, **48**, p. 395–409.  
26 *Preston, El. Review*, 1935, **116**, p. 372.

Cadmium-copper alloys with 99% Cu, 0.9% Cd, and small amounts of Mg (or Si or Li) as deoxidants, can be made as cast to possess over 85% electrical conductivity. They have 10 tons tensile strength, 25% elongation, and a diamond-pyramid hardness of 35–40.

In the copper corner also is an alloy called "hard



Figs. 9 and 10.—Structure of alloy containing 89.8% Cd, 1% Cu, 0.16% Mg.  $\times 100$ .

*Courtesy of John I. Thorneycroft Ltd.*  
**Fig. 12.—Structure of an alloy containing 49% Ag, 22% Cd, 13% Cu and 16% Zn; etched with acid alcoholic 1%  $\text{FeCl}_3$  solution.  $\times 300$ .**

bronze," with 98.5% Cu, 1% Cd and 0.4% Mg, which has been found suitable for welding electrodes. A British patent of the Dutch Molybdenum Co.<sup>28</sup> mentions also that Mg can be replaced by 0.3% Be, and claims an electric welding electrode consisting of a copper alloy containing 1–10% Cd, besides 0.1–5% of one or more of the metals Ag, Mg, Sn, Al or Be.

A photomicrograph of an alloy containing 94.2% Cu, 5.7% Cd and 0.1% Mg belonging to this group of alloys is shown in Fig. 8.

(b) The magnesium corner. Copper-containing magnesium alloys can be modified by the addition of cadmium.

A quaternary electron alloy, AS 82, for forged pistons (DTD 90) contains 8% Al, 2% Si and 0.3% Cu, 1.5% Cd, balance magnesium.

(c) Cadmium corner. Cadmium dissolves up to 0.07% Cu in solid solution. The eutectic alloy, with 1.2% Cu, has a melting point of 314°C. Figs. 9 and 10 show the structure of an alloy containing 89.82% Cd, 1% Cu, 0.16% Mg as cast, and in the annealed condition, respectively. Jenkins<sup>29</sup> investigated cadmium with up to 5% Cu, small additions of magnesium make these alloys into excellent bearing metals. The ternary-bearing metal with 3.1% Cu, 0.2% Mg, balance cadmium, has been described by Gill<sup>30</sup> as of high-class, having a greater hardness, higher melting point and lower coefficient of friction than the tin-base bearing metals. It is used for automobile crankshafts and other bearings.

DTD 217 covers a bearing alloy with 1.3–1.7% Cu, 0.8–1.2% Mg, balance cadmium with maximum 0.75% impurities.

The Bohn Aluminum and Brass Corporation describes in their patent<sup>31</sup> an alloy for bearings consisting of 0.2–1.5% Cu, 0.1–0.75% Mg, balance cadmium, and mentions that for steel back bearings this alloy may contain 0.5% Cu, 0.25% Mg, balance cadmium.

27 Brit. Patent, 350,356.

28 Brit. Patent 156,018 of 1936.

29 *J. Inst. Metals*, 1925, **34**, 103.

30 *Proc. Aust. Inst. Min. Met.*, 1934, **95**, 201.

31 Brit. Patent 439,616 of 1935.

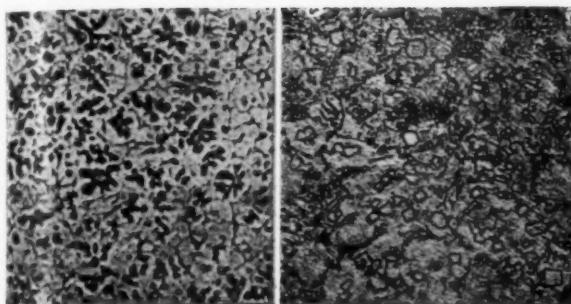


Fig. 13.—Structure of an alloy containing 97.5% Cd, 2.25% Ag, 0.25% Cu, showing primary crystals of Cd (with Ag and Cu dissolved) surrounded by ternary eutectic.  $\times 100$ .

Fig. 15.—Structure of "Asarcloy" containing 98.5% Cd, 1.35% Ni, 0.12% Cu, showing cubic crystals of Cd-Ni in ternary eutectic.  $\times 100$ .

Unfortunately some of these bearing alloys show a tendency to a form of intercrystalline corrosion.

(2) *The System Cd-Cu-Ag (Phase diagram Fig. 11).*—Besides the binary system Cd-Cu, which has been mentioned in the paragraph above, the other two binary systems contained in the ternary system Cd-Cu-Ag are:—

(i) The system Cu-Ag was first established by Heycock and Neville,<sup>32</sup> further investigations have been carried out by Stern-Rainer.<sup>33</sup> The system contains no compound but a eutectic alloy, with 28% Cu and 72% Ag. The solid solubility of silver in copper is about 1%, the solubility of copper in silver about 6%.

(ii) The binary system Ag-Cd has been investigated by Petrenko and Fedorow,<sup>34</sup> and it contains the compounds  $\text{AgCd}_4$  (with 21% Ag),  $\text{AgCd}_3$  (25% Ag), and  $\text{Ag}_2\text{Cd}_3$  (39% Ag). More recent investigations have been carried out by Hume-Rothery<sup>35</sup> and Owen, Rogers and Guthrie.<sup>36</sup>

The ternary system Cd-Cu-Ag has been described by Losana and Goria,<sup>37</sup> but no diagram has been published which is approximately as shown in Fig. 11.

(a) The copper corner. A solid solution of silver and cadmium in copper exists in the little field in the copper corner, and an alloy belonging hereto is covered by a patent of Associated Electrical Industries.<sup>38</sup> The alloy to be used for commutator bars of dynamo machines consists of 95-97% Cu, 0.2-0.3% Ag and 2.7-3.5% Cd.

A British patent of the Dutch Molybdenum Co.<sup>39</sup> claims an alloy of 94.7% Cu, 4% Ag and 1% Cd, with an addition of 0.3% boron, as suitable for the manufacture of welding electrodes and electric make-and-break switch contacts.

A patent of Thomas Bolton and Sons, Mersey Copper Works, Widnes,<sup>40</sup> claims an alloy, "Durode," which can be cold rolled and annealed at intervals, if desired, at 650°-750° C., and finally drawn to give maximum hardness. The composition is 95% Cu, 2.5% Ag and 2.5% Cd. This alloy is especially suitable for electrodes for use in spot-welding and seam-welding, and has a

conductivity of 80% of that of pure copper. "Durode" has a Brinell hardness of 150, and shows great resistance to softening and "mushrooming" during welding operations.

Another British patent,<sup>41</sup> by Bolton and Sons, covers the alloy "Durode XH," with about 1.4% Cd and little or no silver, balance copper, which will be sufficient for spot-welding electrode tips and seam-welding discs, where conditions of service are less severe (resistance to heavy loads at elevated temperatures). Electrodes from such an alloy, hardened to at least 140 Brinell, can be used for about 20,000 spot welds before re-machining or dressing.

(b) The silver corner. In the triangle between pure silver, the compound  $\text{AgCd}_4$  and a copper content of about 6% Cu, there is a field of solid solution of cadmium and copper in silver. These alloys are softer, whiter and more malleable and ductile than silver-copper alloys. As solid solutions they are perfectly homogeneous. This was first pointed out by Kirke Rose of the Royal Mint, who for that reason suggested their use for the preparation of trial plates for assay purposes.<sup>42</sup> The usual composition is 92-92.5% Ag, 7-7.5% Cd, and up to 0.5% Cu.

Sterling silver, used in the United States for silver-ware, is a cadmium-containing silver alloy belonging to this group of alloys.

Ag-Cu-Cd alloys with higher Cd contents are being used for the brazing of copper, e.g., 55% Ag, 40% Cd, 5% Cu, as mentioned by Wyman.<sup>43</sup> This alloy has a melting point of 687° C. and a flow point of 742° C.

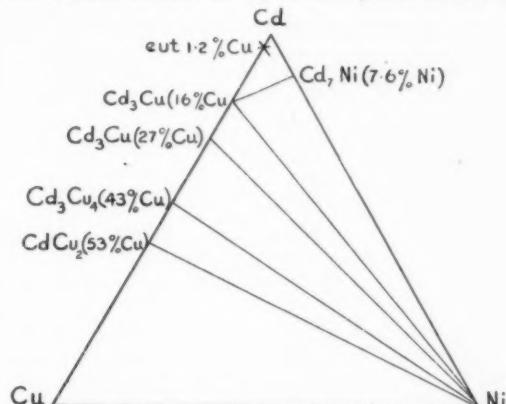


Fig. 14.—Phase diagram of the system Cd-Cu-Ni.

When cadmium is partly replaced by zinc in these alloys, low-melting silver solders are obtained. Investigations on the quaternary system Ag-Cu-Cd-Zn have been carried out by Keinert.<sup>44</sup> An alloy containing 50% Ag, 16% Cu, 18% Cd and 16% Zn has a melting point of 629° C. and a flow point of 637° C. The structure of another alloy of this type is shown in Fig. 12. These alloys are covered by British Standard Specification BSS 206 (silver solders, grade C), and commercial products of similar composition are "Easy Flo" (Johnson, Matthey and Co.) and "Meltesi" (Sheffield Smelting Co.). Low-melting fluxes, mostly containing borofluorides, are being used for the low-temperature brazing with these cadmium-containing silver solders.

<sup>32</sup> Phil. Trans., 1897, **199**, p. 25.

<sup>33</sup> Z. Metallk., 1926, **18**, p. 143.

<sup>34</sup> Z. anorg. Ch., 1911, **70**, 161.

<sup>35</sup> Proc. Roy. Soc., 1937, **100**, p. 282-303.

<sup>36</sup> J. Inst. Metals, 1939, **65**, 457.

<sup>37</sup> Industria Chimica, 1934, **9**, p. 1603.

<sup>38</sup> Brit. Patent 547,080 of 1930.

<sup>39</sup> Brit. Patent 467,162 of 1937.

<sup>40</sup> Brit. Patent 467,259 of 1937.

<sup>41</sup> Brit. Patent 523,424 of 1940.

<sup>42</sup> Metal Ind., Dec. 29, 1939.

<sup>43</sup> Z. Phys. Chem., 1932, **101**, p. 294.

(c) The cadmium corner. The cadmium corner with its nearby eutectic containing 1·2% Cu is very interesting from the practical point of view. Losana and Goria<sup>44</sup> point out that silver and copper contents in cadmium increase its fluidity and reduce considerably the danger of oxidation for cadmium when exposed to the atmosphere. Silver hardens the cadmium, and can partly be replaced in this effect by copper. These cadmium-base alloys are of increasing importance as bearing metals. The alloys near pure cadmium, containing a solid solution of copper and silver in cadmium, are still very soft, but beyond the ternary eutectic with about 1% Cu and 3% Ag, more and more crystals of Cd<sub>3</sub>Cu can be found in the structure, which are hard enough to carry the load.

In the United States a bearing metal is on the market which contains 2·25% Ag, 0·25% Cu, balance cadmium, with a melting point of 321°C. This bearing metal has a Brinell hardness of 40 at room temperature, and still 17 Brinell at 150°C. In Fig. 13 are shown primary crystals containing silver and copper in solid solution embedded in ternary eutectic.

To improve their corrosion resistance, cadmium-alloy bearings can be plated with indium, with consequent heat-treatment to allow the indium to diffuse in completely.

A bearing metal, patented by General Motors,<sup>45</sup> contains 0·05% Ag, 0·25%—1% Cu or Ni, or both, and at least 95% Cd. This bearing metal is not self-bonding, and a bonding alloy for uniting this cadmium-bearing metal to a steel base may consist of 80—95% Cd and 5—20% Zn.

The American Specification SAE 180 gives the following composition for a cadmium-bearing metal—98·25% Cd, 0·5—1% Ag, 0·40—0·75% Cu, and no more than 0·05% impurities consisting of Sn, Zn and Pb.

(3) *The System Cd-Cu-Ni (Phase diagram Fig. 14).*—This ternary system is based:—

- (i) On the already-mentioned binary system Cd-Cu.
- (ii) On the binary system Cu-Ni, which contains neither a compound nor a eutectic alloy.<sup>46</sup>
- (iii) And on the binary system Cd-Ni, established by Voss,<sup>47</sup> containing the only compound Cd<sub>7</sub>Ni with 7·6% Ni. The eutectic between cadmium and the compound Cd<sub>7</sub>Ni contains 0·25% Ni, melting point 318°C, according to Swartz and Phillip.<sup>48</sup>

(a) The copper corner. An alloy practically applied here is covered by a recent patent,<sup>49</sup> with up to 5% Cd, 2—8% Ni (as silicide), balance copper with a slight addition of phosphorus for deoxidation. This alloy is being used for brazing solders, melting rods or electrodes to give hard deposits (200—250 Brinell).

(b) The cadmium corner. The triangle between pure cadmium, the compound Cd<sub>7</sub>Ni (with 7·6% Ni) and the compound Cd<sub>3</sub>Cu (with 16% Cu) contains a field of valuable bearing metals.

A cadmium alloy with 1·35% Ni and little copper (Asarcloy) casts easily, bonds readily to the common backing material, and is not easily oxidised. Its hard constituent, Cd<sub>7</sub>Ni, does not scratch the softest steel. Fig. 15 shows crystals of cubic shape consisting of

Cd<sub>7</sub>Ni, making the structure similar to the Sn-Sb crystals in ordinary white metals, but the compound Cd<sub>7</sub>Ni is much harder than those. For this reason the life of cadmium-alloy bearings is about three times that of other white metals, so far as fatigue cracking is concerned. They show good corrosion resistance as long as the actual bearing temperature does not rise above

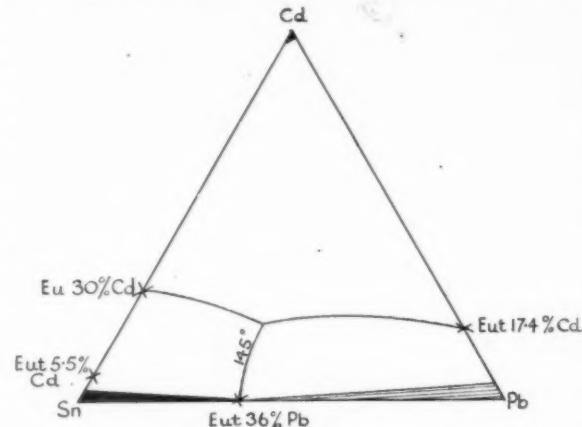


Fig. 16.—Phase diagram of the system Cd-Sn-Pb.

130°C., and if only highly refined mineral oils (free from sulphur compounds) are used, having an addition of corrosion inhibitors as organic phosphites, etc. This alloy also is not self-bonding, and an alloy with 80% Cd and 20% Zn is used for this purpose.

The American specification, SAE 18, for cadmium-base automobile bearings has the composition 98·5% Cd, 1—1·5% Ni, up to 0·1% Cu, with no more than 0·01% each of Sn, Zn and Pb.

Another alloy with 97% Cd, up to 3% Ni and up to 0·3% Cu, at temperatures up to 200°C., has double

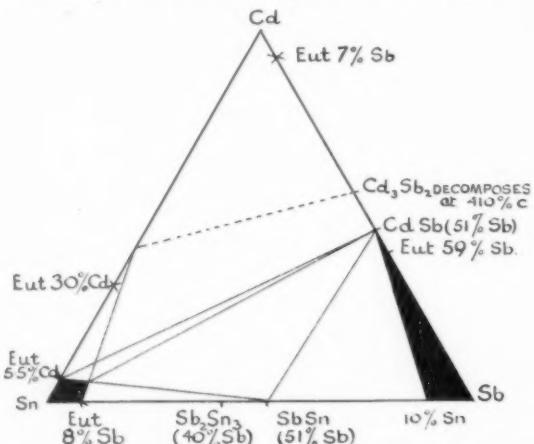


Fig. 17.—Phase diagram of the system Cd-Sb-Sn.

the tensile strength of good white metal. It bonds directly to steel and bronze without forming an intermetallic compound between the bearing metal and the shell. For this reason there is less danger of the bearing metal separating on account of poor adhesion, especially as its ductility is very high.

<sup>44</sup> *Chimica e l'Industria*, 1935, **17**, 159.

<sup>45</sup> Brit. Patent 436,633 of 1935.

<sup>46</sup> Z. anorg. Ch., 1907, **52**, p. 27.

<sup>47</sup> Z. anorg. Ch., 1908, **57**, p. 70.

<sup>48</sup> Am. Inst. Min. Met. Eng., 1934, **111**, p. 333.

<sup>49</sup> Brit. Patent 535,673 of 1941.

### Group C.—Cadmium Alloys with Sn-Pb, Sn-Zn and Sn-Cu.

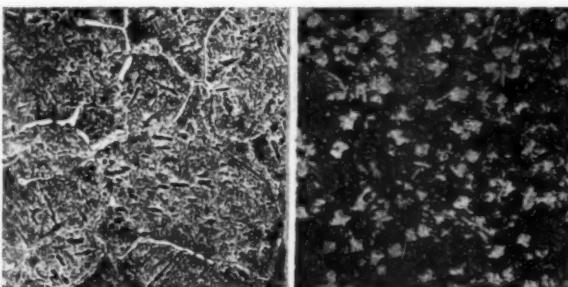
*The System Cd-Sn-Pb (Phase diagram Fig. 16).*—This ternary system is based on three binary systems:—  
(i) The system Cd-Sn, which is fully established. Latest publications are by Hanson and Pell Walpole.<sup>50</sup>

There is no intermetallic compound, the solid solubility of tin in cadmium is only 0·25% Sn. A eutectic alloy exists with 70% Sn. and 30% Cd. On the tin side there is a solid solubility up to 1% Cd, but alloys containing up to 5·5% Cd, balance tin, have a eutectoid transition at 128° C. for practically all tin-cadmium alloys.

(ii) The system Cd-Pb, established by Rollason and Hysel,<sup>51</sup> contains a eutectic alloy with 82·6% Pb and 17·4% Cd (melting point 248° C.).

(iii) The binary system Sn-Pb contains no intermetallic compound but a eutectic alloy with 36% Pb and 64% Sn (melting point 181° C.).

(a) The tin corner. Nothing of practical importance has been found in the tin corner itself, but an alloy consisting of 50% Sn, 25% Cd and 25% Pb (melting point 149° C.) is being used as a low-melting, very liquid solder for tin foils in the manufacture of electrical condensers. An alloy with 33% Cd, 67% Sn and little lead (near the eutectic) has been tried as a dental alloy (melting point 176° C.).



(From Hanson and Pell Walpole.)

Fig. 18.—Structure of alloy containing 92% Sn, 3% Cd, 5% Sb, quenched from 195° C., etched in acid  $\text{FeCl}_3$ .  $\times 300$ .

(From Lurgi-publications, 1938, p. 28.)

Fig. 19.—Structure of alloy containing 89% Sn, 1.4% Cd, 9.6% Sb.  $\times 100$ . Primary cuboids of Sb-Sn on dark matrix.

(b) The lead corner. A B.N.F.M.R.A. patent<sup>52</sup> covers a lead-base alloy for cable sheathing (B.S.S. 801, of 1938) with the following composition:—0·35–0·45% Sn, 0·12–0·18% Cd, 99·4% Pb (alloy C). Another alloy in the lead corner is the B.N.F. ternary alloy No. 2, which is specified by B.S.S. 603 of 1941 for lead pipes. It contains 1·25–1·75% Sn, 0·2–0·3% Cd, and 98–98·5% Pb.

An alloy with about the same composition (1·5% Sn, 0·25% Cd, balance lead) can be used as a very low-tin "plumber's solder." Higher contents of Sn and Cd in lead for use as soft solders were used during the last war with 7·5% Cd, 5% Sn, balance lead,<sup>53</sup> here as well as in Germany, where a "German soft solder," with 10% Sn, 10% Cd and 80% Pb, was used to save tin (melting point 200° C.).

A recent patent by the National Lead Co.<sup>54</sup> claims a hardened lead alloy with 4·5% Sn, 1% Cd, balance lead, with 0·08% Ca as a primary hardener.

Two early American patents covered a bearing alloy, "Touceda metal," with 8–18% Cd, 0·5% Sn, balance lead, with a melting range of 255°–280° C.

(c) Cadmium corner. A fusible alloy, "Clichiermetal," with a melting point of only 105° C., has a composition of 56% Cd, 22% Pb and 22% Sn.

(2) *The System Cd-Sn-Zn.*—Investigation on this ternary system have been carried out by Lorenz and Plumbridge.<sup>55</sup> An alloy of this system is being used as a soft solder for aluminium and has a composition of 40% Sn, 40% Zn and 20% Cd.

(3) *The System Cd-Sn-Cu.*—Nothing has been published on this system. For the time being only alloys in the copper corner are of practical importance. These alloys are a variation of the Cd-Cu alloys, where cadmium, being an intermediate between zinc and tin, is partly replaced by tin, e.g., 0·5% Cd, 0·5% Sn, balance copper. These "conductivity bronzes" have the following mechanical properties:—Annealed—18 tons tensile strength, 60% elongation, 54 Brinell; hard—35 tons (wire up to 45 tons), 5% elongation, 110 Brinell.

### Group D.—Cadmium Alloys with Sb-Sn, Sb-Pb and Sb-Zn.

*(1) The System Cd-Sb-Sn (Phase diagram Fig. 17).*—This ternary system is based on the following binary systems:—

(i) The system Cd-Sn, which has been mentioned before in Group C.

(ii) The system Cd-Sb, which is of importance for all the ternary alloys of this group. It has been established by Kurnakow and Konstantinow<sup>56</sup>; more recent investigations have been carried out by Murakami and Shiragawa<sup>57</sup> and Abel, Halla and Redlich.<sup>58</sup> There are two intermetallic compounds, Cd-Sb and  $\text{Cd}_3\text{Sb}_2$ , and two eutectic alloys with 7% Sb and 93% Cd (melting point 290° C.) and 59% Sb and 41% Cd (melting point 455° C.).

(iii) The system Sb-Sn, established by Hanson and Pell Walpole,<sup>59</sup> contains the intermetallic compounds  $\text{Sb}_2\text{Sn}_3$  with 40·5% Sb and Sb-Sn with 51% Sb. A eutectic alloy with 8% Sb exists between pure tin and the compound  $\text{Sb}_2\text{Sn}_3$ .

(a) The tin corner. The technically applied alloys in the tin corner are in the field which is limited on one side by the eutectic containing 5·5% Cd, on the other side by the eutectic containing 8% Sb. This field is that of the ternary tin-rich solution alpha in the system Sn-Cd-Sb, according to the constitution diagram established by Hanson and Pell Walpole.<sup>60</sup>

The alloy with 3% Cd, 7% Sb, balance tin, melting point 236° C., balance tin is the hardest of these lead-free tin-base bearing metals. Its mechanical properties are 7 tons tensile strength, 25% elongation, and 35 Brinell, and the alloy will withstand 50% reduction by cold-rolling. An alloy with lower Sb content is shown in Fig. 18.

53 Hill, *Metal. Ind.*, 1918, 10.

54 Brit. Pat. 518,775 of 1941.

55 Z. anorg. Ch., 1913, 83, p. 228.

56 Z. anorg. Ch., 1908, 58, p. 16.

57 Japan, 1928.

58 Z. anorg. Ch., 1928, 174, 257; 1932, 205, p. 398; and 1933, 214, p. 196.

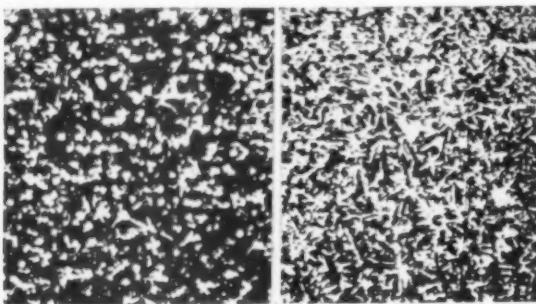
59 J. Inst. Metals, 1936, 58, p. 299.

60 J. Inst. Metals, 1937, 61, p. 265 and 443–485.

If copper and small amounts of nickel are introduced as further components, one arrives at the lead-free bearing metals covered by DTD 214 containing up to 5% Cd, 6.5-7.5% Sb and 3-4.5% Cu, besides up to 0.5% Ni. The purpose of the nickel addition is to reduce possible segregation in the structure by forming crystals of  $\text{NiSb}$  and  $\text{Ni}_3\text{Sn}_2$ .

Alloys suitable as bearing metals can also be found outside the alpha field in the tin corner. Thus, Fig. 19, reproduced from "Lurgi-publications, 1938," shows the white phase of  $\text{SbSn}$  (containing some tin and cadmium) in a matrix of dark ternary tin-rich solution alpha. The alloy has a composition of 9.6% Sb, 1.4% Cd, balance tin.

**Quaternary alloy Cd-Sb-Sn-Cu:** The complete change of structure caused by the addition of only 1% Cd to a copper-containing tin-base bearing metal can be seen in the two photomicrographs shown in Figs. 20 and 21, which have been published by Greenwood.<sup>61</sup>



(From Greenwood, "J. Inst. Met., 1934, 55, 49.)

Fig. 20.—Tin-base bearing metal (96% Sn, 10% Sb, 4% Cu).  $\times 100$ .  
Fig. 21.—Tin-base bearing metal (85% Sn, 10% Sb, 1% Cd, 4% Cu).  $\times 100$ .

**(2) The System Cd-Sb-Pb (Phase diagram Fig. 22).**—This system is quasibinary with  $\text{Cd}_3\text{Sb}_2$  as hardening constituents in the lead. Up to the present only the lead corner of this system is of practical importance. Solid solutions do not exist here, but the intermetallic compound  $\text{Cd}_3\text{Sb}_2$  (long needles) forms a eutectic with lead containing 91% Pb and 9% of the cadmium antimony compound.

An alloy with 0.45-0.55% Sb, 0.2-0.3% Cd and 99.25% Pb is covered by a B.N.F. patent,<sup>62</sup> and is recommended for cable sheathing by B.S.S. 801 of 1938, alloy D. A similar alloy has been recommended by the B.N.F.M.R.A. as lead-pipealloy. An alloy with 1.2% Cd, 1.5% Sb, balance lead, can be used as bearing metal.

Further additions of tin to these ternary alloys have made it possible to develop a wide range of bearing metals with better hardness and higher impact strength. These quaternary alloys, which have all the advantages of the hardening effect of the Cd-Sb system, are superior to the Sn-Sb-Pb bearing metals, especially in their resistance to frictional wear.

Further additions of copper and nickel assist in reducing possible segregation, because their intermetallic compounds with tin and antimony solidify first when the bearing metals cool down to the solidus line, and they form a network which prevents segregation.

In this system are the following alloys: Bondrat bearing metal (Metallhuette Liesing, Austria) with 10% Sb, 1% Cd, 2% Cu, 1% As, 10% Sn, balance lead. Thermit bearing metal (Goldschmidt, Essen) with 14-16% Sb, 0.7-1.5% Cd, 0.8-1.2% Cu, 0.7-1.5%

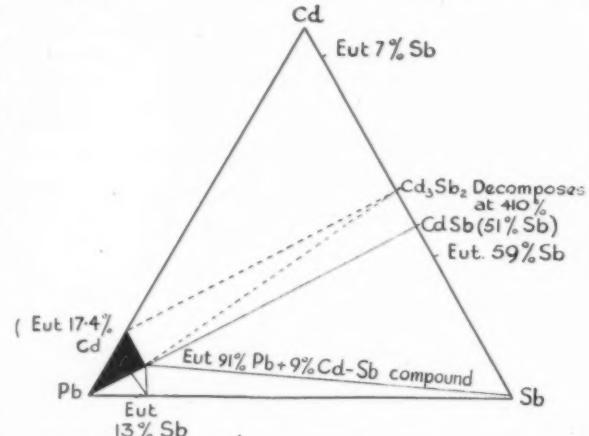


Fig. 22.—Phase diagram of the system Cd-Sb-Pb.

Ni, 5-7% Sn, 0.2-0.8% As, balance lead. EEL anti-friction metal (Murex, Rainham) with 15% Sb, 1.5% Cd, 1% Cu, 1% Ni, 6% Sn, balance lead.

Additions of zinc to the ternary system Cd-Sb-Pb lead to bearing metals containing hard crystals of the compound  $\text{Zn}_3\text{Sb}$ . Cook<sup>63</sup> found that this is of disadvantage for the bearing life of the alloy, as this

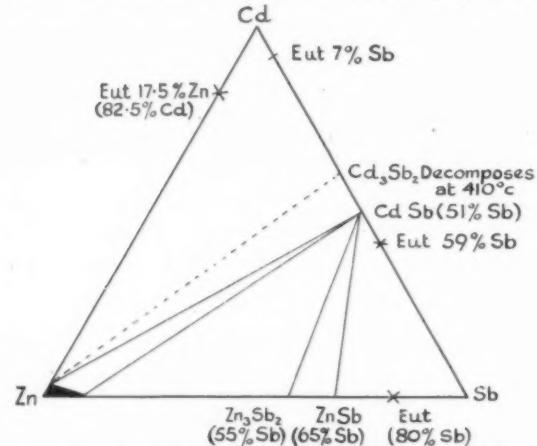


Fig. 23.—Phase diagram of the system Cd-Sb-Zn.

compound has the tendency to transform itself into the brittle compound  $\text{ZnSb}$ .

Nevertheless, alloys of this type have later on been claimed by two United States patents<sup>64</sup> with 18% Cd, 10% Sb, 5% Zn, balance lead, and with 7.5% Cd, 7.5% Sb, 3% Zn, balance lead.

**(3) The System Cd-Sb-Zn (Phase diagram Fig. 23).**—

In the zinc corner is an alloy with up to 4% Cd, 0.2% Sb (or Hg), balance zinc, which is covered by a patent<sup>65</sup> as suitable for battery electrodes.

61 J. Inst. Metals, 1934, 55, p. 49.

62 Brit. Patent 272,320.

63 J. Inst. Metals, 1924, 31, p. 297.

64 Am. Patent 1,745,314 of 1930 and 1,807,670 of 1931.

65 Brit. Patent 429,547 of 1930.

Many attempts have been made to make the binary Zn-Cd alloys, which can be used as solders (DTD 221A with 70% Zn and 30% Cd), or Cazin solder (with 82.5% Cd, balance zinc), into bearing metals by additions of antimony. An early alloy of this type is the Siemens bearing metal<sup>66</sup> with 47% Cd, 5% Sb, balance zinc. More recently an American patent<sup>67</sup> claimed a bearing metal consisting of 78% Cd, 5% Sb, balance zinc.

#### Group E.—Cadmium Alloys with Bi-Sn and Bi-Pb.

(1) *The System Cd-Bi-Sn.*—This system has been established by Stoffel<sup>68</sup>, and a practically applied ternary alloy is Newton's metal with 21% Cd, 53% Bi and 26% Sn (melting point 103° C.). The introduction of cadmium into bismuth-containing alloys lowers their melting point quite considerably and leads to the

"fusible alloys," most of which will melt in hot water.

(2) *The System Cd-Bi-Pb.*—This system has been established by Barlow<sup>69</sup>, and a practically applied ternary alloy consists of 68% Cd, 31.5% Bi and 0.5% Pb with a melting point of 70° C., used as filler for tube bending.

(3) The quaternary system Cd-Bi-Sn-Pb has been investigated by Parravano and Sirovich.<sup>70</sup> Here belong most of the fusible alloys used for safety plugs, clichées and soft solders, for automatic electrical cutouts and thermometric alarms. Examples are Lipowitz metal with 10% Cd, 50% Bi, 13% Sn and 27% Pb (melting point 70° C.) and Wood metal with 12.5% Cd, 50% Bi, 12.5% Sn and 25% Pb. (melting point 60.5° C.).

(4) A modern variation of the Lipowitz metal contains an addition of indium, whereby the melting point is brought down to only 46° C. The composition of this quaternary eutectic alloy is 8% Cd, 41% Bi, 10.5% Sn, 22% Pb and 18% In.

<sup>66</sup> German Patent 176,886 of 1906.  
<sup>67</sup> Am. Patent 1,864,240 of 1932.  
<sup>68</sup> Z. anorg. Ch., 1907, **53**, 167.

<sup>69</sup> J. Am. Chem. Soc., 1910, **32**, 1,390.  
<sup>70</sup> Gazz. Chim. it., 1911, **41**, p. 655; and 1912, **42**, p. 630.

## Thermodynamic Considerations in the Corrosion of Metals\*

By Professor J. C. Warner

*The available thermodynamic data are reviewed and used to calculate the spontaneity of corrosion reactions for most of the common metals in deoxygenated water and in water saturated with carbon-dioxide-free air. The results of such calculations are summarised for the common metals in several environments. If the actual corrosion process is spontaneous, the conditions for the steady state limiting corrosion rate by setting the free energy decrease in the process equal to the sum of the energies dissipated in the various parts of the electrochemical system.*

MOST metals and alloys of engineering importance, when attacked by one of the common environments, aqueous media in absence of air, aqueous media in the presence of air, moist air, or aqueous media containing various anions, quickly saturate the environment with a compound of the metal, and a solid corrosion product is deposited near the point of attack. If the environment is composed of only water, oxygen and nitrogen ( $\text{CO}_2$  and other reactive substances absent), the solid-corrosion product must be the oxide, hydrated oxide, or hydroxide of the metal. If anions other than the hydroxyl ion are present in the aqueous environment, the solid-corrosion product may consist of the normal or basic salts of the metal with these anions, if the formation of these corrosion products is more spontaneous than the formation of the hydroxide or oxide of the metal. Thus, with  $\text{CO}_2$  in the atmosphere, or with carbonates or bicarbonates in the aqueous environment, one must examine the possibility of producing normal or basic carbonates as the corrosion product; with chloride, sulphate, chromate, phosphate, etc., in the aqueous environment, the possible production of normal or basic salts of the metal with these anions must be considered.

The best compilations of thermodynamic data, which have been searched for the data necessary for making a calculation of the spontaneity of a specific corrosion reaction, were: (a) the International Critical Tables<sup>2</sup>; (b) Kelley's Bulletins of the U.S. Bureau of Mines<sup>3</sup>; (c) Bichowsky and Rossini's<sup>4</sup> "Thermochemistry of Chemical Substance," and (d) Latimer's<sup>5</sup> "Oxidation Potentials." For possible revisions of the data given in these compilations, and for new data, the later periodical literature was consulted.

In general, the thermodynamic properties of the common metals, water, oxygen, hydrogen and carbon dioxide are well known. The principal difficulties are encountered in obtaining satisfactory data on the metal compounds which constitute the solid-corrosion products. One can find moderately reliable data on most metal oxides, most normal carbonates, some metal hydroxides, and some other normal salts. There are few reliable data, however, on basic salts and on some of the metal hydroxides.

As all physical chemists know, one may obtain the free energy change (measure of the spontaneity) in a

<sup>2</sup> International Critical Tables, McGraw-Hill Book Co., Inc., New York (1930).

<sup>3</sup> K. K. Kelley, U.S. Bureau of Mines, "Contributions to the Data on Theoretical Metallurgy," Bulletin No. 350, 371, 383, 393, 394, 406, 407, 434.

<sup>4</sup> F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York (1936).

<sup>5</sup> W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York (1938).

\* Based on material presented at the American Association for the Advancement of Science Symposium on Corrosion, August, 1942, and presented at the recent general meeting of the Electrochemical Society at Pittsburgh. (Preprint 83-5.)

chemical reaction in any one of three general ways:  
(1) From actual experimental measurements which give the equilibrium constant:

$$\Delta F^\circ = -RT \ln K$$

where  $\Delta F^\circ$  is the standard free energy change, R the gas constant, T the absolute temperature, and K the equilibrium constant.

(2) From a knowledge of the absolute entropies of all substances involved in the reaction and the heats of formation of the compounds involved:

$$\Delta F^\circ = \Delta H - T\Delta S^\circ$$

where  $\Delta H$  is the heat of reaction and  $\Delta S^\circ$  is the standard entropy change in the reaction.

(3) From reversible oxidation potentials or single electrode potentials for electrode reactions which can be combined to give the overall corrosion reaction:

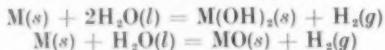
$$\Delta F^\circ = -nFE^\circ$$

where n = number of equivalents reacting and F is the value of the Faraday—i.e., 23,066 cal. per volt equivalent. In corrosion reactions this method of determining  $\Delta F^\circ$  will require that we know the standard electrode potential of the metal and the solubility (activity) of the slightly soluble corrosion product.

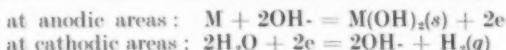
### Corrosion by Water in Presence and Absence of Oxygen

A summary has been prepared of the thermodynamic data on the corrosion reactions of the common metals in two common environments: (a) the metal in contact with water in the absence of oxygen, and (b) the metal in contact with water saturated with oxygen at a partial pressure of 0.21 atmosphere (air).

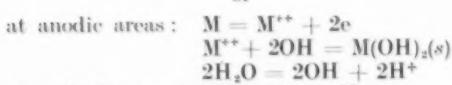
In the former of these cases solid metal, M(s), must be oxidised by displacing hydrogen, and we are therefore concerned with reactions of the type:



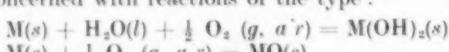
Reactions of this class are referred to as "Hydrogen Type," H<sub>2</sub>(g), representing gaseous hydrogen. If the process is electrochemical, the total reaction may be divided into its anodic and cathodic parts as follows:



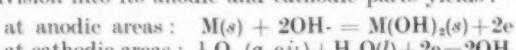
or



In the latter of the above cases (referred to as "Oxygen Type"), metal is oxidised by oxygen in the air diffusing into solution to the cathodic areas, and one is concerned with reactions of the type:



A division into its anodic and cathodic parts yields:



A summary of the estimated best values of the free energy change per mole of metal oxidised and of the corresponding reversible (maximum) potentials of the corrosion couples is given in Table I.

TABLE I—SPONTANEITY OF CORROSION REACTIONS.\*

Metal	Solid Product,†	Hydrogen Type at PH <sub>2</sub> = 1.0 atm.		Oxygen Type at PO <sub>2</sub> = 0.21 atm.		Footnotes.
		E <sub>a</sub>	ΔF per g-mole metal, cal.	E	ΔF per g-mole metal cal.	
Mg	Mg(OH) <sub>2</sub>	+ 1.823 volt	- 84,000	+ 3.042 volt	- 140,000	6, 7
Al	Al(OH) <sub>3</sub> (?)	+ 1.48	- 102,570	+ 2.70	- 180,700	8
Mn	Mn(OH) <sub>2</sub>	+ 0.60	- 27,600	+ 1.81	- 83,200	9, 10
	Mn(OH) <sub>3</sub>	+ 0.256	- 16,700	+ 1.50	- 103,000	11
	MnO <sub>2</sub>	+ 0.14	+ 12,700	+ 1.11	- 101,000	12, 13
Cr	Cr(OH) <sub>3</sub>	+ 0.47	- 32,500	+ 1.69	- 117,000	14
Zn	Zn(OH) <sub>2</sub> (?)	+ 0.417	- 19,240	+ 1.636	- 75,200	15, 16, 17, 18, 19, 20, 21
Fe	Fe <sub>3</sub> O <sub>4</sub>	+ 0.082	- 5,020	+ 1.30	- 80,000	22, 23, 24, 25
	Fe(OH) <sub>2</sub>	+ 0.049	- 2,200	+ 1.27	- 58,500	26
	Fe(OH) <sub>3</sub>	- 0.07	+ 4,700	+ 1.15	- 80,000	27
Cd	Cd(OH) <sub>2</sub>	- 0.013	+ 600	+ 1.206	- 55,600	28, 29, 30
Co	Co(OH) <sub>2</sub>	- 0.098	+ 4,500	+ 1.12	- 51,700	31, 32
Ni	Ni(OH) <sub>2</sub>	- 0.17	+ 7,800	+ 1.05	- 48,500	33
Pb	Pb(OH) <sub>2</sub>	- 0.250	+ 11,500	+ 0.97	- 44,600	34, 35, 36, 37
Cu	Cu <sub>2</sub> O	- 0.413	+ 9,500	+ 0.800	- 18,600	38, 39
	Cu(OH) <sub>2</sub>	- 0.604	+ 27,800	+ 0.615	- 28,300	40
Hg	HgO	- 0.557	+ 24,800	+ 0.680	- 31,450	39
	Hg <sub>2</sub> O	- 0.926	+ 42,600	+ 0.293	- 13,600	41
	Hg <sub>2</sub> O	- 0.951	+ 21,970	+ 0.268	- 6,190	41
Ag	Ag <sub>2</sub> O	- 1.172	+ 27,000	+ 0.047	- 1,080	36, 42, 43, 44, 45

\* Brown, Roetheli and Forrest probably were the first investigators to attempt a summary of this type. They also used the terms "Hydrogen Type" and "Oxygen Type" in the same sense as they have been used in this paper, *Ind. Eng. Chem.*, **23**, 350 (1931).

† Except when the formula is followed by (?), the data given are quite certainly for the formation of the solid corrosion product which is the most stable solid phase in contact with water. The formulae given do not, in any case, attempt to indicate the extent of hydration of the stable solid phase.

### Discussion of Table

It is evident that all of the metals listed in Table I will be attacked by water saturated with air to form solid-corrosion products—i.e., the corrosion reaction is spontaneous even when the environment is saturated with the corrosion product. Since this is a common practical case, we can understand why we have so many problems connected with controlling corrosion rates. Of the metals included, Mg, Al, Mn, Cr, Zn and Fe can react with water in the absence of free oxygen to form a solid-corrosion product. Manganese cannot be oxidised to MnO<sub>2</sub>(s) by water, and Mn(OH)<sub>2</sub> is the most stable solid phase produced by the attack of deoxygenated water on this metal. Mn(OH)<sub>3</sub> is a more stable solid phase

6 R. Nasanen, *Z. physik. Chem.*, **A188**, 273 (1941).

7 Latimer (see footnote 5), p. 272.

8 Latimer, p. 263.

9 Latimer, p. 219.

10 R. K. Fox, D. F. Swinehart and A. B. Garrett, *J. Am. Chem. Soc.*, **63**, 1779 (1941).

11 Latimer, p. 221.

12 W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," p. 370, The Macmillan Co., New York (1940).

13 Latimer, p. 22.

14 Latimer, p. 230.

15 Latimer, p. 155, 156.

16 H. G. Dietrich and J. Johnston, *J. Am. Chem. Soc.*, **49**, 1119 (1927).

17 G. C. Bauer, *Iowa State College J. Sci.*, **13**, 37 (1938).

18 Bichowsky and Rossini (see footnote 4).

19 K. K. Kelley, U.S. Bur. Mines Bull. No. 437 (1941).

20 E. A. Anderson and M. L. Fuller, *Metals and Alloys*, **10**, 282 (1939).

21 F. R. Moral, *Trans. Electrochem. Soc.*, **77**, 279 (1940).

22 J. Chipman and D. W. Murphy, *Ind. Eng. Chem.*, **25**, 319 (1933).

23 O. C. Ralston, U.S. Bur. Mines Bull. No. 296 (1929).

24 R. C. Corey and T. J. Finnegan, *Proc. Am. Soc. Testing Materials*, **39**, 1,257 (1939).

25 M. deK. Thompson, *Trans. Electrochem. Soc.*, **78**, 251 (1940).

26 M. Randall and M. Frandsen, *J. Am. Chem. Soc.*, **54**, 40, 47 (1932).

27 Latimer, p. 210, 211.

28 H. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2,624 (1936).

29 Latimer, p. 159.

30 M. Quintin, *Compt. rend.*, **208**, 1,564 (1938).

31 Latimer, p. 199.

32 A. Grosser, *Compt. rend.*, **205**, 383 (1937).

33 Latimer, p. 188.

34 A. B. Garrett, S. Vellenga and C. M. Fontana, *J. Am. Chem. Soc.*, **61**, 367 (1939).

35 Latimer, p. 140.

36 K. Farago, *Chem. Abstr.*, **32**, 2,033 (1938).

37 J. J. Lingane, *J. Am. Chem. Soc.*, **60**, 724 (1938), *2*.

38 L. M. Adams and D. J. Brown, *J. Am. Chem. Soc.*, **59**, 1,387 (1937).

39 Kelley, U.S. Bur. Mines Bull. No. 434 (1941) and Ref. 4.

40 Latimer, p. 174.

41 Latimer, pp. 161-165.

42 G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York (1923).

43 B. B. Owen, *J. Am. Chem. Soc.*, **60**, 2,229 (1938).

44 J. J. Lingane and W. D. Larson, *J. Am. Chem. Soc.*, **58**, 2,647 (1936).

45 K. S. Pitzer and M. V. Smith, *J. Am. Chem. Soc.*, **59**, 2,633 (1937).

than  $Mn(OH)_2$  or  $MnO_2$  in the "Oxygen Type" corrosion of manganese. This, however, does not rule out the possibility of a solid phase such as  $Mn_3O_4$  being more stable than  $Mn(OH)_3$ . The oxidation of  $Mn(OH)_2$  to  $Mn(OH)_3$  by  $H_2O$  is not spontaneous:

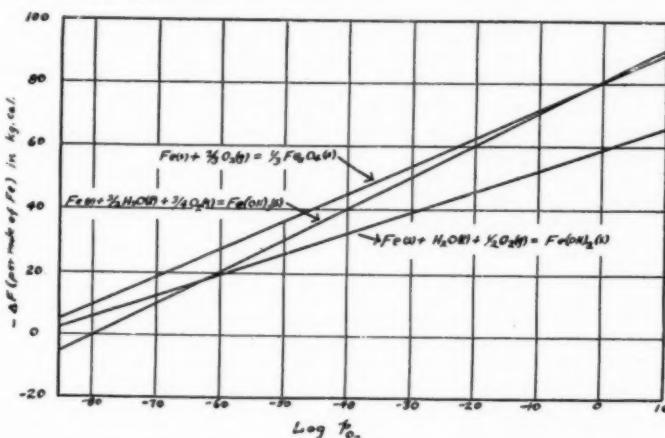
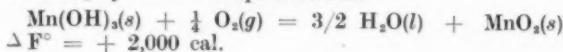
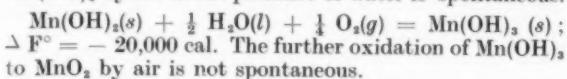
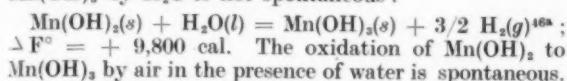
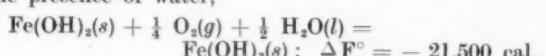


Fig. 1.—Showing the spontaneities of the various corrosion reactions of iron as a function of the oxidising power of the aqueous environment.

Dearated water can attack iron to form ferrous hydroxide or magnetite. The latter is the most stable solid phase, but the formation of  $Fe(OH)_2$  as an intermediate phase is entirely possible. The reaction leading to the formation of a solid phase of ferric hydroxide is non-spontaneous in dearated water; but in aerated water this may be considered the most stable solid phase. However, there is little difference between the stability of  $Fe_3O_4$  and  $Fe(OH)_3$  as solid phases when  $pO_2 = 0.21$  atm.; any slight difference obtained in calculations is smaller than the uncertainty of the available data. The spontaneities of the various corrosion reactions of iron as a function of the oxidising power of the aqueous environment are well illustrated in Fig. 1. At oxidising powers equivalent to that of air ( $p/pO_2 = 0.21$  atm.), the reactions leading to  $Fe_3O_4$  and to  $Fe(OH)_3$  are about equally spontaneous; that leading to  $Fe(OH)_2$  is much less spontaneous. As the oxidising power of the aqueous environment is increased,  $Fe(OH)_3$  formation becomes the most spontaneous reaction. At all oxidising powers less than that equivalent to air, the formation of  $Fe_3O_4$  remains the most spontaneous reaction. At an oxidising power equivalent to  $p/pO_2 = 10^{-63}$  atm., the formation of  $Fe(OH)_2$  becomes equal in spontaneity to the formation of  $Fe(OH)_3$ . Finally, at an oxidising power equivalent to  $pO_2 = 10^{-65}$  atm., the formation of  $Fe(OH)_3$  is not spontaneous. This last situation is interesting because it represents the oxidising power of water saturated with hydrogen gas at 1 atm. pressure—i.e., it is the environment we have specified for the "Hydrogen

Type" corrosion of iron. It is a necessary conclusion from the data that  $Fe(OH)_2$  will spontaneously change to  $Fe_3O_4$  with the evolution of hydrogen; that  $Fe(OH)_2(s)$  cannot be oxidised to  $Fe(OH)_3$  by water; that  $Fe(OH)_2(s)$  can be oxidised to  $Fe(OH)_3$  by air in the presence of water,



and that  $Fe_3O_4(s)$  can probably be oxidised to  $Fe(OH)_3$  by air in the presence of water.

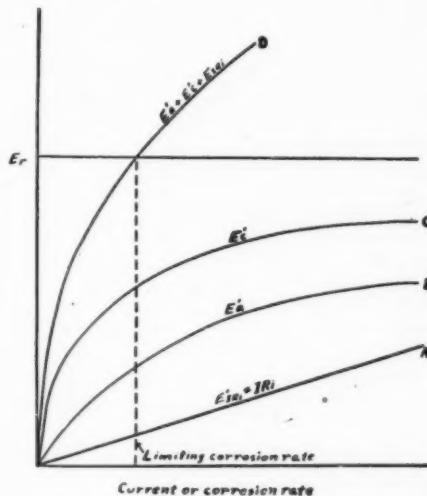
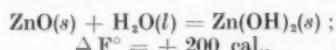


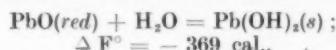
Fig. 2.—Showing graphically the significance of the limiting corrosion rate.

In attempting to summarise data on corrosion reactions for some of the metals, one encounters the problem of whether the hydration of the oxide to the hydroxide is a spontaneous process—i.e., whether the oxide or the hydroxide of the metal represents the more stable solid phase is not a simple one. There is little question but that the hydroxides of Ag, Hg and Cu are unstable with respect to the oxides and liquid water at ordinary temperatures. The cases of Zn and Pb are interesting. One can calculate for



but this value of  $\Delta F^\circ$  is less than the uncertainties in the available data. One may therefore assume that  $ZnO(s)$  and  $Zn(OH)_2(s)$  are about equally stable as solid phases in contact with aqueous media, and it is not surprising<sup>20, 21</sup> that both ZnO and  $Zn(OH)_2$  have been found as constituents of the corrosion products of zinc.

There is abundant evidence that the red modification of  $PbO$  is the stable form at ordinary temperatures. From available data one can calculate for



indicating that the hydroxide is a more stable solid phase than  $PbO(red)$ . However, the value of  $\Delta F^\circ$  again is less than the uncertainty in the data from which it was derived. The recent careful work of Garrett, Vellenga and Fontana<sup>34</sup> shows that the solubility of  $PbO(red)$  in water and in alkaline solutions is less than

the solubility of white precipitated lead hydroxide. Indeed the solubilities of the white hydroxide are practically identical with those of yellow PbO. One must conclude, therefore, that red PbO represents the most stable solid product of the "Oxygen Type" corrosion of lead, and our calculation of the spontaneity has been based on this assumption.

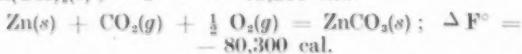
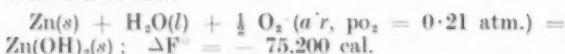
Similar difficulties are encountered with the calculations on reactions of iron leading to the formation of a ferri-corrosion product. The thermodynamic data upon which the values in Table I are based are for the precipitated ferric hydroxide and are not very precise. It seems likely that a partially hydrated ferric oxide (i.e.,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , where  $x < 3$ ) is more stable in the presence of liquid water than ferric hydroxide. If this is true, it would favour the formation of  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  over  $\text{Fe}_3\text{O}_4$  as the solid product in the "Oxygen Type" corrosion of iron.

A conclusion of importance is that the free energy of hydration of some of these oxides is so small that the difference in energy between a stable crystalline material and a freshly precipitated finely divided material may be of the same order of magnitude as the energy of hydration. Thus, the hydration of finely divided amorphous  $\text{ZnO}(s)$  might be spontaneous and the hydration of stable crystalline  $\text{ZnO}(s)$  non-spontaneous. One may therefore expect to observe changes in the character of the solid corrosion product with small changes in the conditions under which it is formed in many instances.

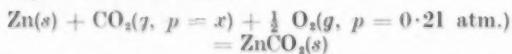
### Other Corrosion Reactions

In many instances thermodynamic data are available for calculating the spontaneity of the reaction whereby specific metals are corroded in specified environments other than those which have been defined for "Oxygen Type" and "Hydrogen Type" corrosion. A summary of other "Type" reactions has not yet been undertaken, but a brief discussion of a few additional cases may be interesting and useful.

A very common environment to which metals are exposed is one consisting of water or aqueous solutions saturated with air containing carbon dioxide. The thermodynamic properties of the normal carbonates of the common metals are pretty well known, and it therefore would be possible to summarise values of the spontaneities of corrosion reactions of the metals in the presence of aqueous media saturated with air containing any specified partial pressure of  $\text{CO}_2$ . An interesting summary would be one which gave the partial pressures of  $\text{CO}_2$  in the atmosphere required to make the formation of the normal carbonate as corrosion product as spontaneous as the formation of the oxide or hydroxide. At partial pressures of  $\text{CO}_2$  in excess of this value one would expect the carbonate as corrosion product. As an example one may make such a calculation for the corrosion of zinc.



If one calculates the  $p_{\text{CO}_2}$  which will make  $\Delta F^\circ = -75,200$  for the reaction—

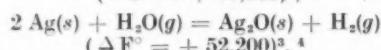
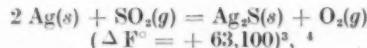


one obtains  $x = p_{\text{CO}_2} = 3.9 \times 10^{-4} \text{ atm.} = 0.30 \text{ mm.}$

corresponding to 0.039% or 390 p. p. m. of  $\text{CO}_2$  in the atmosphere. This is higher than the average (300 p. p. m.), but is within the range (200 to 440 p. p. m.) of values reported for the  $\text{CO}_2$  content of clean country air<sup>47</sup>; it is lower than the range of values reported (400 to 800 p. p. m.) for the  $\text{CO}_2$  content of urban and industrial atmospheres.<sup>47</sup> The above calculation, together with the reported data on the seasonal, weekly and daily fluctuation in the  $\text{CO}_2$  content of the atmosphere indicate that zinc in many practical environments may be expected to form oxide or hydroxide during certain parts of the exposure time and may form carbonate as the corrosion product during other portions of the exposure.

These conclusions should be applied with considerable caution for two reasons: (1) the thermodynamic data are not sufficiently precise to fix  $p_{\text{CO}_2} = x$ ; thus, an error of 500 cal. in  $\Delta F^\circ$  means an error of 0.17 mm. in  $p_{\text{CO}_2}$ . (2) There is considerable evidence that under certain conditions encountered in practice, various basic carbonates of zinc, or solid solutions of the carbonate in the hydroxide, represent more stable solid phases than the normal carbonate or hydroxide.<sup>48</sup> There is notable lack of agreement,<sup>48</sup> concerning the constitution of the solid corrosion product which is formed when zinc is exposed to aqueous environments in the presence of air. For this reason, there is an urgent need for experiments in which the environment is carefully controlled during the exposure and the corrosion products are subjected to chemical X-ray diffraction, electron diffraction, and other methods of analysis.

Another interesting set of corrosion reactions are those which may be involved when silver is exposed to air containing sulphur vapour, sulphur dioxide, or hydrogen sulphide. The various reactions which one should consider as possibilities are listed, along with the corresponding standard free energy changes ( $\Delta F^\circ$ ), in Table II. Two reactions which one might imagine namely,



are ruled out of consideration because they are so non-spontaneous.

TABLE II.—FORMATION OF SILVER SULPHIDE AND SILVER SULPHATE.

Reaction.	$\Delta F^\circ$ at 25° C. <sup>6</sup>
1. $2 \text{Ag}(s) + \text{S}(rh) = \text{Ag}_2\text{S}(s)$	— 8,700 cal.
2. $2 \text{Ag}(s) + \text{H}_2\text{S}(g) = \text{Ag}_2\text{S}(s) + \text{H}_2(g)$	— 800
3. $2 \text{Ag}(s) + \frac{1}{2} \text{O}_2(g) = \text{Ag}_2\text{O}(s)$	— 2,450
4. $2 \text{Ag}(s) + \text{H}_2\text{O}(g) = \text{Ag}_2\text{O}(s) + \text{H}_2\text{O}(g)$	— 55,500
5. $2 \text{Ag}(s) + \text{S}(rh) + 2 \text{O}_2(g) = \text{Ag}_2\text{S}(s) + \text{O}_2(g)$	— 146,800
6. $2 \text{Ag}(s) + \text{H}_2\text{S}(g) + 2 \text{O}_2(g) = \text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(g)$	— 193,600
7. $2 \text{Ag}(s) + \text{SO}_2(g) + \text{O}_2(g) = \text{Ag}_2\text{S}(s) + \text{SO}_3(g)$	— 75,000
8. $1 \text{Ag}(s) + 2 \text{SO}_2(g) = \text{Ag}_2\text{S}(s) + \text{Ag}_2\text{SO}_4(s)$	— 12,000
9. $\text{Ag}_2\text{S}(s) + 2 \text{O}_2(g) = \text{Ag}_2\text{SO}_4(s)$	— 138,100,
10. $\text{Ag}_2\text{O}(s) + \text{S}(rh) = \text{Ag}_2\text{S}(s) + \frac{1}{2} \text{O}_2(g)$	— 6,250
11. $\text{Ag}_2\text{O}(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{Ag}_2\text{SO}_4(s)$	— 72,600
12. $\text{Ag}_2\text{O}(s) + \text{H}_2\text{S}(g) = \text{Ag}_2\text{S}(s) + \text{H}_2\text{O}(g)$	— 53,000

\* Values of  $\Delta F^\circ$  are based on data from footnotes 3 and 4.

It seems certain that the principal products of the corrosion of silver in urban and industrial atmospheres are silver sulphide and silver sulphate.<sup>49</sup> From Table II

<sup>46</sup> Kelley, U.S. Bur. Mines, Bull. No. 384.

<sup>46a</sup> Unless gas pressures are given, it is implied that the gas is at 1 atm. pressure;

<sup>47</sup> F. N. Speller, "Corrosion—Causes and Prevention," p. 167, McGraw-Hill Book Company, New York (1935); J. R. S. Haldane, *Nature*, **137**, 575 (1936);

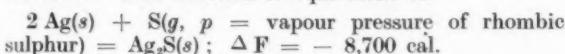
T. M. Carpenter, *J. Am. Chem. Soc.*, **59**, 358 (1937).

<sup>48</sup> M. F. Taboury and E. Gray, *Compt. rend.*, **205**, 985 (1937); Bull. Soc. Chim., **1**, 368 (1939); E. A. Anderson and M. L. Fuller, *Metals and Alloys*, **10**, 282 (1939); F. R. Morral, *Trans. Electrochem. Soc.*, **77**, 279 (1940).

<sup>49</sup> Based on private discussions with W. E. Campbell.

it is evident that there are a variety of spontaneous reactions whereby these products could be formed when silver is exposed to air containing small amounts of sulphur vapour, hydrogen sulphide or sulphide dioxide. Which of these possible reactions are responsible for the attack will depend very much upon their relative speeds, and one would suspect that the adsorption coefficients of  $O_2$ ,  $S$ ,  $H_2S$ ,  $SO_2$  and  $H_2O$ , as well as the concentrations of these substances in the atmosphere, would be involved in the problem.

Experiments which have been brought to the author's attention indicate that Reaction (1) may be quite important in the production of a sulphide tarnish film on silver. This reaction is equivalent to



The vapour pressure<sup>50</sup> of rhombic sulphur at 25°C, is reported in the range  $(0.4 \text{ to } 8.0) \times 10^{-6} \text{ mm.}$ , which permits one to calculate that sulphur vapour at any partial pressure above  $(1.0 \text{ to } 20.8) \times 10^{-12} \text{ mm.}$  could attack silver to form sulphide. Another interesting

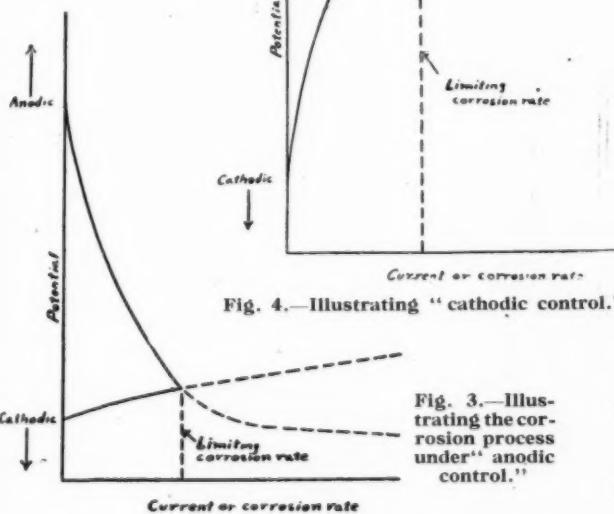


Fig. 4.—Illustrating "cathodic control."

Fig. 3.—Illustrating the corrosion process under "anodic control."

calculation is that of finding the partial pressure of sulphur vapour which would make the formation of sulphide as spontaneous as the formation of oxide in air ( $p_{O_2} = 160 \text{ mm.}$ ). The result shows that at any partial pressure of sulphur in air higher than  $(0.6 \text{ to } 33.0) \times 10^{-11} \text{ mm.}$ , the formation of the sulphide is more spontaneous than the oxide. This partial pressure is only  $1/158,000$  the vapour pressure of sulphur at 25°C.

#### The Steady State or Limiting Corrosion Rate

If the proposed or actual corrosion process is spontaneous and proceeds by an electrochemical mechanism one may state the conditions for the steady state or limiting corrosion rate by setting the energy decrease in

the process equal to the sum of the energies dissipated in the various parts of the electrochemical system. For convenience in discussing the conditions for the steady state, the energy liberated and the various energies dissipated in the process may be converted into potentials. This is, in a way, analogous to the application of Bernoulli's theorem to fluid flow problems.

The reversible potential of the corrosion couple may be considered the driving force of the process, and the steady state corrosion rate will be the rate that makes the sum of all the dissipative effects, expressed as counter-electromotive forces, equal to the driving force. Hence for the steady state one may write

$$E(\text{reversible}) = \sum E'(\text{dissipative}).$$

If one writes the equation to show the terms which make up the sum, it becomes

$$E_r = E'_a + E'_c + E'_{IRi} + E'_{IRe}$$

where

$E_r$  = reversible electromotive force of the couple (Table I).

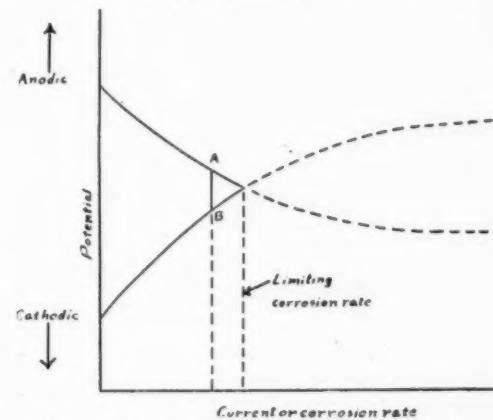


Fig. 5.—Representing an example of mixed control.

$E'_a$  = total polarisation at the anode areas.

$E'_c$  = total polarisation at the cathode areas.

$E'_{IRi} = IR_i$  = current flowing  $\times$  resistance of electrolyte between cathode and anode areas.

$E'_{IRe} = IR_e$  = current flowing  $\times$  resistance of the metal between cathode and anode areas. This resistance,  $R_e$ , ordinarily is very small and hence  $E'_{IRe}$  may be neglected in most cases.

It is important to note that all of the dissipative terms making up the right-hand side of the above equation are functions of the current density. The significance of the limiting corrosion rate may be demonstrated graphically by reference to Fig. 2.

Curve D represents the sum of A, B and C. When corrosion proceeds at a rate corresponding to a current  $I$  flowing between anodic and cathodic areas, the sum of the irreversible or dissipative effects (total polarisation) is equal to the driving force of the corrosion couple. Therefore, a rate corresponding to the current  $I$  will be the steady-state corrosion rate if the character of the overall corrosion reaction is not changed. From the

<sup>50</sup> International Critical Tables, Vol. III, p. 201; K. K. Kelley, U.S. Bur. Mines, Bull. No. 406 (1940).

diagram it should be evident that anything that will increase the resistance of the electrolyte, increase the total anodic polarisation, or increase the cathodic polarisation, will decrease the corrosion rate. This conclusion is very useful in any endeavour to find a means of decreasing the corrosion rate in a given system.

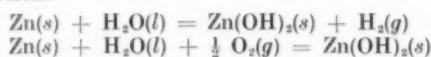
In most cases  $E_c$  and  $E_s$  are large compared to  $E'_{IRI}$  and one may consider that polarisation makes anode areas less anodic and cathodic areas less cathodic. Thus as polarisation increases, the two areas are being brought more nearly to the same potential. If  $E'_{IRI}$  may be neglected, the corrosion rate that will yield sufficient polarisation to bring the anodic and cathodic areas to the same potential will be the limiting corrosion rate. This scheme is illustrated in Fig. 3, 4 and 5.

The difference between the potential of the anode and the cathode at zero current represents the reversible electromotive force or driving force of the corrosion couple. As the rate of discharge of the couple is increased, the potentials (including polarisation) of the anode and cathode approach each other, and become equal at the limiting or steady-state corrosion rate. If  $E_{IRI}$  has an appreciable value, the corrosion rate is set at a lower limit, namely, the rate at which  $E_{IRI}$  is equal to the difference between the anodic and cathodic curves. In Fig. 5 I represents the limiting rate if  $E_{IRI}$  is very small, but I' is the limiting rate when  $E_{IRI} = AB$ .

If, as is illustrated in Fig. 3, anodic polarisation is the predominant dissipative effect, the corrosion process is said to be under "anodic control." The case illustrated in Fig. 4, obviously, is under "cathodic control."

Fig. 5 represents an example of "mixed control," in which anodic and cathodic polarisations are comparable in magnitude. In any attempt to apply protective measures it usually is important to recognise the type of control that prevails in the unprotected case.<sup>51</sup>

This treatment of the steady state corrosion rate is rather obviously an over-simplification because cases are well known in which the corrosion of a metal or alloy proceeds by two or more simultaneous processes. In such cases a steady state equation would apply to each process, and the total rate of attack would be the sum of the steady state rates for the separate processes. For example, the hydrogen type as well as the oxygen type corrosion of zinc is spontaneous in aerated water. Hence zinc can be attacked simultaneously in the reactions



A steady state equation would apply to each reaction and the total rate of attack on zinc would be the sum of the rates permitted in the separate reactions.

Finally, it should be emphasised that the irreversible dissipative effects which appear on the right-hand side of the steady state equation are not related to the overall free energy change in the corrosion reaction. Therefore, one has no reason to expect a correlation between corrosion rate and the overall driving force for the process.

<sup>51</sup> L. C. Bannister and U. R. Evans, *J. Chem. Soc.*, 1930, 1,361; Evans, Bannister and S. C. Britton, *Proc. Roy. Soc.*, 131, A, 355 (1931).

## National Fuel Economy

### The Importance of Auxiliary Gas-firing

**A** CONSIDERABLE economy in coal can be obtained by using to the best advantage every description of low-grade fuel that is available for the operation of steam boilers, including, for example, small coal and coke breeze, as well as general industrial, canteen, household and similar refuse. During recent years great advances have of course been made in water-tube boiler practice, both in the power station and the industrial field, with the efficient burning of two or more fuels together in one combustion chamber. Such fuels include coal and coke (both by means of mechanical stokers and pulverised fuel equipment), peat, wood, petroleum sludges, coal tar and coal-tar fractions (including pitch), natural gas, town gas, coke-oven gas, producer gas, and blast-furnace gas.

The scientific principle, however, apart from iron and steel works is largely neglected as regards ordinary industrial boiler plants. Thus, in many cases when low-grade fuels are being used, along with coal, such as coke breeze and wood waste from pattern shops, the results obtained are deplorable as regards thermal efficiency because of low combustion chamber temperature, due largely to defective equipment. In this connection auxiliary gas-firing, even when using town gas, quite apart from producer gas, coke-oven gas, and blast-furnace gas, is often an economical proposition which increases considerably the combustion efficiency of the solid material.

For this purpose, of particular interest is the range of "Gako" turbulent burners supplied by Liptak Furnace Arches, Ltd., which are available in a considerable number of sizes and modifications, although the basic

principles are the same in each case. Essentially, they consist of separate and independent valve control of the gas and air supply, which are also split up in the burner into a number of independent thin layers or streams, each of which is given a twisting or whirling motion by means of spiral guides or passages. The result is an extremely intimate mixing of the gas and the air, with rapid completion of the combustion, giving a short globular flame with high  $\text{CO}_2$  and little excess air. Another feature is that the operation is under low-pressure conditions, generally 2-4 in. w.g., which eliminates all "stratification"—that is, non-uniform furnace temperature—which is apt to be one of the inherent troubles of high-pressure burner operation.

All the designs also are characterised by simplicity and accessibility, with no moving parts of any kind. One valuable general method of application is to fit these burners as auxiliary to solid fuel firing by hand at the top of the combustion chamber over the grates, operating the burner by the natural draught. Thus, in the case of "Lancashire" and other cylindrical boilers, the burners are fitted at the top of the furnace tubes above the firedoors, whilst in the case of small or medium size water-tube boilers, low-pressure forced draught burners are fitted for auxiliary firing in conjunction with mechanical stokers, or, of course, for gas-firing only. Another important development in this connection with these burners is to use forced draught by means of an integral fan and electric motor, giving a performance equal in efficiency and convenience to the very largest power station water-tube boilers. By this means the operation of the burners is independent of the chimney or other induced draught and the arrangement lends itself particularly well to automatic control of gas supply in accordance with the varying demand for steam.

# New Laboratories of the British Cast-Iron Research Association

*The above laboratories were officially opened by Lord Riverdale on May 28, 1943, before a considerable number of members and visitors, after which the premises were inspected. Brief reference is made to the speeches made at the opening ceremony and to the laboratories.*

FOLLOWING the last great war the iron foundry industry encountered a severe slump; much progress had been made in the replacement of iron castings by the welding of mild steel sections, and it was feared by many that the general trend of development was operating to the disadvantage of this industry. It is probable that the lack of proper organisation of the iron casting industry contributed to the depression which then existed, not only in the production of iron castings but in the condition of mind of many of the executives within the industry.

That this position has changed, and for many years past the outlook has been more promising, is largely due to the excellent work done by the British Cast-Iron Research Association, which was instituted when the morale of the industry was at a low level. This Association, by steady but persistent work, has imbued the industry with a new spirit, and gradually new uses for cast iron have been developed and extended and its progress has been accelerated by war conditions. While the need for improved organisation still exists, many problems peculiar to this industry have been tackled in a profitable manner. Intensive research and development work has not only increased the scope of cast iron, but it seems to have lifted the industry out of its despondency, and to-day it is more alive than ever before to the need for improvements in iron castings to meet the higher standards modern conditions demand.

From a relatively small beginning the British Cast Iron Research Association, which rented its first laboratory in 1924, has gradually grown in spite of formidable difficulties. In 1926 the offices and laboratories were combined under one roof in St. Paul's Square, these were subsequently enlarged on three occasions. In April, 1941, the Council decided to move, and Bordesley Hall was found during the summer of that year. Funds collected during the presidency of Lord Dudley, while adequate for removal and adaptation of the premises, proved to be inadequate for their acquisition, and the president, Mr. P. Pritchard, undertook the negotiations for the purchase and lent the purchase money, since repaid.

Bordesley Hall, shown in the accompanying illustration, is situated about twelve miles from Birmingham in grounds which cover about 15 acres. This country house, set in charming surroundings, is now the headquarters of the British Cast-Iron Research Association, where a competent staff under the direction of Mr. J. G. Pearce will continue their work on the problems of the cast-iron industry, and its development; work from which, stated the president, Mr. P. Pritchard, at the official opening, will result in cast iron being provided in forms and shape and for uses as yet undreamed of.

The new venture was officially opened by Lord Riverdale of Sheffield, Chairman of the Advisory Council



Bordesley Hall.

of the Department of Scientific and Industrial Research, before a considerable number of members and visitors. He was supported by Lord Dudley, Regional Commissioner for the Midland Area and a past-president of the Association, and by Sir Edward Appleton, secretary of the Department of Scientific and Industrial Research.

Formally opening the new headquarters, Lord Riverdale described the occasion as a great step forward. He had no doubt that the facilities the laboratories provide will assist the cast-iron industry to meet problems of both home and export trade after the war. At the present time the work carried out is mainly concerned with the war effort, but it will also have applications for post-war developments. He made it clear that the future of industry in this country, and in particular the dependence of industry on research, are engaging the attention of authoritative bodies concerned with the future prosperity of this country, and there is no doubt in their minds of the necessity for extending research and the means for using and applying science in industry.

Lord Dudley expressed himself rather caustically regarding facilities that were all too often placed at the disposal of research workers, and briefly described the efforts made to improve these facilities. From these new headquarters he looked forward to a vast improvement and development in the scientific application of cast iron. British industry would be faced with formidable difficulties after the war; these could only be overcome by using to the utmost the brains and genius of the country. It could not be done without the application of scientific development. He had been privileged to see something of what scientists and research workers had accomplished in the war effort, and he was astounded at the success achieved. These efforts must be continued

after the war in order that industry may be placed in an advantageous position to recover the world's markets. The laboratory must become the most important part of the workshop; unless this is fully appreciated and acted upon we shall not live as an industrial nation.

That the Association had the full support of the Department of Scientific and Industrial Research was emphasised by Sir Edward Appleton, who believed it would markedly extend its research after the war. It has been said that while Britain had been responsible for many notable discoveries in pure science, other nations usually applied the results. That may have been true in the past, but matters will be very different after the war. Sir Edward said he had seen the results of British scientists on the practical problems of war-time, and assured members and visitors that they can apply their science to a practical thing in a manner which can at least match the efforts of any other nation, and science can be harnessed equally well to peace as to war. There will be a great forward movement in applying science to industrial needs after the war, and no sound research project will lack financial support from the Government.

Dr. Harold Hartley, chairman of Council, in thanking the various speakers referred briefly to the work of the Association. Arrangements were then made for the inspection of the premises; the ground floor comprising the administrative offices, library and information bureau and development department. The first floor houses the microscopic, physical metallurgy, sands and refractories, and vitreous-enamelling laboratories. Outbuildings contain the machine shop and mechanical testing laboratory, chemical laboratory, and experimental foundry.

#### Departmental Organisation

Apart from the general and administrative offices the Association is organised in three main sections—the Library and Information Bureau, the Research Department, and the Development Department. Both the latter departments are aided by a group of laboratories, brief reference to which will be of interest.

*Sands and Refractories Laboratory.*—This laboratory is equipped for tests on refractories, core and moulding sands, binders and auxiliary materials. Sand preparation is carried out in a 10-lb. Simpson mixer, and mechanical composition, or grading, is determined by a battery of electriators and standard B.S.I. sieves shaken by a Sinex vibrator. Green strength and permeability are measured by the Association's designs of compression tester and permeability apparatus. Dry sands are tested on a standard type cement tester, and for baked core sands a hydraulic machine capable of applying loads up to 3 tons will be installed. Cores are baked in a thermostatically controlled oven with internal air circulation. High-temperature tensile tests are furnished

by the Rees-Chesters apparatus. Sands and apparatus can also be examined microscopically, and for sintering and melting points, gas-fired Brayshaw furnaces, going up to 1,600° to 1,700° C., are located in the experimental foundry.

*Physical Metallurgy Laboratory.*—This laboratory is used for cooling curve determinations, dilatometric tests, experimental heat-treatment and pyrometric calibration, and in addition to the usual electrical instruments is equipped with a Carpenter-Stansfield

#### The Library and Information Bureau.



#### The Chemical Laboratory.

potentiometer, recorders for noble- and base-metal thermocouples and muffle and tube furnaces. A Gale dilatometer, a platinum-wound tube furnace and lead bath are being added, and apparatus for measuring magnetic properties and resistivity obtained. An electronic dilatometer and muffle furnace are under construction.

*Metallographic Laboratory.*—This laboratory is equipped for the preparation, examination and recording of metal structures at any magnification, as well as equipment for ordinary photography and the production of negatives, prints, enlargements and duplicates in quantity. Two dark rooms are used. The laboratory proper contains modern polishing machines, visual

microscopes and the latest design of Vickers' projection micro-camera, fitted with a comprehensive range of eyepieces, objectives, light filters and polarising apparatus. An optical lantern is also available with equipment for preparation of lantern slides. A press for mounting specimens in plastic material is being obtained.

*Finishing Process and Vitreous Enamelling Laboratory.*—This laboratory is concerned with the techniques of and problems arising in connection with finishing processes, and particularly vitreous enamelling. Both wet and dry process enamel can be made, prepared and applied on a small scale. Apparatus for metal preparation, mixing, melting, grinding, and sieving enamel is installed. Enamel can be applied by dipping, spraying or dry dusting. An electric furnace is used for annealing, firing enamel and determination of enamel softening points and flow properties. Colour and reflectance of enamels can be measured, as well as resistance to impact and chemical attack, the latter tests devised in the laboratory.



The Experimental Laboratory.

*Machine and Instrument Shop.*—Sampling for chemical analysis, microscopic examination, and preparation of test-pieces for mechanical and physical testing are carried out in the machine shop, where apparatus within the capacity of the equipment available is made. Three drilling machines, a Ward 7-in. all-gearied lathe and two rough turning lathes, a Myford 3-in. centre lathe are available, with two mechanical saws capable of taking metal up to 8-in. thick, with tools for general construction and repair. An abrasive cutting wheel is used for white and very hard iron. The equipment is being supplemented by a milling machine and a shaper.

*Mechanical Testing Laboratory.*—This laboratory is equipped for the conduct of mechanical tests, transverse, tensile, compression, hardness, impact, damping capacity. The machines include a 50-ton Avery universal and 10-ton Denison machine; Brinell, Rockwell and diamond hardness testing machines; the Izod impact and the Cambridge damping capacity machine. A Tensometer tensile testing machine is available for very small test-pieces. Equipment is being obtained for fatigue testing, creep testing and short-time tests at elevated temperatures.

*Chemical Laboratory.*—This laboratory is concerned with chemical determinations and is equipped with the usual fume cupboards, muffle furnaces, titration bench, drying ovens and stills, and combustion trains for carbon determination. A platinum-rhodium wound furnace is also used for combustion sulphur determinations. The balance-room contains two balances of the "chainomatic" type for rapid weighing, a semi-micro balance and three other accurate balances. Apparatus is also available for determining oxides in pig and cast irons by aqueous iodine, total oxides by aluminium reduction. There is also a portable pH meter and a Lovibond colorimeter. To this is being added an electrodeposition apparatus fitted for potentiometric titration, a Spekker photoelectric absorptiometer, vacuum fusion, and vacuum heating apparatus for determining gases and total oxides in iron and steel, and a Hilger quartz spectrograph with accessories.

*Physical Laboratory.*—The acquisition of an X-ray tube for the study of appropriate materials by electron diffraction is under consideration, and will probably be housed in a small separate building with the spectrograph and equipment for determining mechanical properties at elevated temperatures.

*Experimental Foundry.*—The foundry is equipped for moulding, melting and casting, and has a Simpson sand mill and core stove by the Foundry and Engineering Co., Ltd. Shot-blast equipment is shortly to be added. Shatter tests on coke can be made. The melting furnaces include a coke-fired crucible furnace for melting small charges, 25–100 lb.; an oil-fired Morgan tilting furnace for charges of 200–300 lb. A Cura type of coke-fired tilting furnace for charges up to 200 lb. is also installed but is not yet in commission. The melting furnace equipment also includes a constructional cupola, a

rocking arc Birlee-Detroit furnace, and a small high-frequency Efcō induction furnace for melting charges up to 10 lb. The cupola is of 12 in. diameter, and has a capacity of 700–800 lb. of fluid metal per hour, while the electric rocking furnace is conveniently used with a 50–80-lb. metal charge.

Other furnaces include heat-treatment furnaces and gas-fired furnaces for sintering, and other tests on refractory materials. The Birlee heat-treatment furnace can be used for heat-treatment cycles up to 1,000° C. on castings of varying dimensions. A further furnace is on order for annealing temperatures up to 1,100° C., fitted with a programme controller, by means of which the metal may be submitted to any annealing cycle, completely predetermined with respect to both temperature and duration of the heating cycle. An electrically salt-bath furnace for temperatures up to 950° C. is also on order.

There can be no doubt that the movement of this Association to more commodious premises and the determination of its Council to equip and staff the

laboratories to enable the industry to draw to the fullest extent on these services will increase its usefulness. Certainly, the services to be rendered after the war are likely to be considerable. To maintain and increase its position, however, requires a greatly increased

income, and since the results of the work done directly, or indirectly, affects every iron foundry in the country, it should be regarded as a sound business proposition to be a member of this Association, so that full advantage can be taken of close collaboration within the industry.

## Solubility of Metals in Mercury

**A**MONG the uses of mercury is the making and breaking of electrical circuits, and since the circuit terminals involve other metals also, an accurate knowledge of the interaction of mercury and such other metals is of considerable importance. Most metals dissolve slightly in mercury, and also react with it to form intermetallic compounds. Platinum is embrittled under prolonged contact with mercury. Iron and tungsten appear inert, but the effect may, it is considered, be partially due to protection afforded by adherent surface films of oxide. Lead, tin, zinc, and cadmium are sufficiently soluble to alter the properties of the mercury, which makes them unsuitable for use in contact with it in mechanical devices. Silver, copper, nickel and platinum are only slightly soluble.

Studies of the solubility of silver, copper, nickel, platinum, iron and stainless steel have recently been made by a new method which is described in a paper by C. H. Prescott,\* an abstract of which is given in the current issue of the *Nickel Bulletin*† and is reproduced here. The method involves the use of a circulating still of pyrex glass. Mercury is evaporated from a boiler into a condenser and subsequently flows down through a bulb packed with scraps of the metal, the solubility of which is being determined, and thence back into the boiler. Since the mercury moves slowly, it becomes saturated with metal, which subsequently precipitates in the boiler. After a few days, or months, depending on the solubility of the metal under test, the still is removed from the thermostat, the mercury completely evaporated from the boiler, and the residue recovered for chemical analysis. This residue is the metal dissolved, at the temperature of the thermostat, in the total amount of mercury circulated during the experiment. The stills used are not adapted to measure the rate of circulation, but it was possible to estimate that about 1 kilog. of mercury circulated per day in each of these experiments, since the mercury siphons intermittently through the return tube.

Due to the uncertainty of this estimate, solubilities so derived are accurate only within a factor of three. They are nevertheless interesting in indicating very clearly marked differences in the solubilities of the various metals. The solubility of silver was found to be 0.0018 grm. per gram of mercury, while that of copper was only 0.00013 grm. per gram. The experiments on these metals required three and thirteen days respectively. Determinations on nickel and platinum, which were very much less soluble, required three and seven months respectively. The nickel residue was small, and

the platinum recovered was a mere speck. The solubility of nickel was  $1.4 \times 10^{-7}$  grm./grm., or one part in seven million. That of platinum was thirty times less,  $4.6 \times 10^{-9}$  grm./grm.

With iron and stainless steel, the boilers were perfectly clean after eight months. Washings gave a spectroscopic test for iron, with indicated solubilities of about  $5 \times 10^{-11}$  grm./grm., or one part in twenty billion. This finding may indicate a true solubility, or may be due to an invisible particle of scale which drifted into the boiler. Although further work would be required to establish a quantitative result, it may be stated with certainty that the solubilities of iron and of stainless steel are extremely small. (The paper includes an illustration of a solenoid valve which has been added to the still, to measure the flow of mercury.)

A further feature of importance in connection with the use of mercury in contact with other metals is the wetting of the surfaces and the effect of the fluid film of mercury left on them. At the surface of contact a layer of solid amalgam is formed. Silver amalgam forms readily; copper, soaked in mercury for a few months at 100° C. disintegrates completely into crystals of copper amalgam. The surfaces of nickel, which has been submerged a few days, and platinum, a few months, become rough and granular, and when the mercury is distilled off, layers of nickel- or platinum-black are left. These consist of finely divided metal particles formed by disintegration of the solid amalgam. (A nickel surface covered with nickel black is illustrated in the original.) It thus appears that the material in equilibrium with mercury in the solubility experiments is not the metal itself, but a layer of solid amalgam. The metal must be regarded as more soluble than the amalgam, and as it slowly dissolves it is re-precipitated as an intermetallic compound, which covers the surface and retards further attack. The free metal is essentially unstable in the presence of mercury, and the change into solid amalgam is one form of disintegration suffered by silver, copper, nickel and platinum. The solubilities of nickel and platinum are below the limit of a spectroscopic test on the mercury in equilibrium with the metal and the quantity of metal actually in the mercury, at any instant, is negligible. It appears, however, that there are relationships between solubility and the rate of disintegrative processes which affect the service life of mercury switches. These processes include the formation of solid amalgam and, in some cases, intercrystalline attack of the metal itself.

The sensitivity and simplicity of the method described in the paper is considered to render it adaptable for wide use in low-solubility determinations.

\* C. H. Prescott, *Bell Laboratories Record*, 1942, vol. 21, pp. 104-7.

† Vol. 16, No. 5.

# The Mineral Monazite

By L. Sanderson

*Two elements, thorium and cerium, which have long been regarded as rare metals, but which are increasing in importance, are produced from the mineral monazite, and in this article the author gives some data concerning these metals and briefly describes their extraction from this mineral.*

**M**ONAZITE is the mineral mainly used in commercial practice for the production of the metallic element thorium. It is made up primarily of phosphates of the cerium and lanthanum earths with, in addition, a fluctuating percentage of thoria. It has a specific gravity of 4.8 to 5.5, and is a yellow-gold to reddish brown mineral, which has also been found dark brown or black in tint. The chemical formula is  $(CeLaDi) PO_4$ , with a thoria ( $ThO_3$ ) content ranging between 3 and 10%. In addition to its thorium content, this mineral is also the only important source of cerium. It derives its name from a Greek word meaning "to be solitary," for the reason that it was at one time considered to be an extremely rare mineral.

Monazite occurs in a number of gneissic and granitic rocks, but most of the commercially exploited deposits are of alluvial character. Large monoclinic prisms up to a foot in length are found in pegmatite, and small yellow grains are found in gneiss. The alluvial deposits are composed of the disintegrated rock fragments washed down by heavy rains into pools and streams and, along with other heavy sands, forming a sedimentary deposit in river beds. In Brazil, monazite deposits are found in the sands off the sea coast, where they have been washed down from the crystalline mountain rocks. In small streams and river beds the mineral is usually found in the form of gravel. It is often associated with ilmenite, garnet, zircon and rutile. Separation of the mineral from these associates can readily be effected by magnetic means, strong magnetic fields removing the ilmenite and garnet, weaker fields eliminating the zircon and rutile.

The main sources of monazite are Brazil and India, but some quantities have been produced in the United States of America. It has also been located in Switzerland, Africa and Australia, and to a minor degree in the rocks of Ekaterinburg, Russia. In Brazil its principal source is the sea beaches of the States of Bahia and Espírito Santo; in India, the beaches of Travancore, between Muttum and Coluchil, in Southern India, yield the major quantities; in the United States the worked deposits exist in the Carolinas, Idaho and Florida. Some monazite has been found in the Cingalese sands, in the Federated Malay States, and in the Dutch East Indies.

Few actual figures of production are obtainable, but according to the latest publication of the Imperial Institute, India produced 2,628 long tons in 1936, 3,081 in 1937, and 5,221 in 1938, a steady increase. It is probable that as a result of war conditions, still further increases have been made in production. The only figures available for Brazil are those of her exports, which represented 417 tons in 1937 and 318 tons in 1938. The Dutch East Indies produced 657 long tons in 1936, 364 in 1937, and 387 in 1938. Egypt, which produced 1 ton in 1936, has produced nothing since.

Thorium, one of the principal metals produced from monazite, has an atomic weight of 232.15, while its melting-point is in the region of  $1,800^{\circ}C$ . The atomic number is 90. It is a lustrous, dark metal with a specific gravity of 11 to 12, and burns in air below a red heat to produce the dioxide. In addition to monazite, thorite and thorite contain it, and minor amounts have been obtained from these sources, which are, however, greatly restricted. Thorite is a silicate ( $ThSiO_4$ ) containing 48.7% of thorium oxide,  $ThO_2$ . Thorium is radioactive.

Cerium, the other element obtained from monazite, has an atomic weight of 140, and its atomic number is 58. In appearance it bears a striking resemblance to iron. Its melting-point is  $546^{\circ}C$ , and it has a specific gravity of 70. Malleable and ductile, it is not a good conductor of electricity, readily tarnishes when exposed to the air, ignites in air, and gives a brighter flame even than magnesium when made into wire.

The extraction of thorium from monazite embodies a number of secret processes, all of which have undergone considerable evolution as a result of local conditions, fluctuation in the cost of chemicals, and so forth. The basis of the processes, as far as it is known, is as follows: The monazite is mixed with about double its own weight of concentrated sulphuric acid and heated up in cast-iron receptacles until at a certain point decomposition of the monazite is complete. The residuum is a white aggregation of sulphates that are insoluble in the acid. The mixture is transferred to a vat lined with lead and water is added, the entire mass being agitated until it has completely dissolved. After this it is permitted to stand for a sufficient time to allow of the slow deposition on the vat bottom of the insoluble particles of silica, zircon, rutile, etc. The liquor remaining, in which are contained the phosphatic matter and rare earths, is then decanted, and the free acid neutralised to some extent to make it less active. This causes a precipitation out of thorium phosphate, which is less soluble than the other phosphates.

This precipitation still carries small amounts of the other phosphates, and for this reason it is carefully filtered, dissolved in the smallest possible quantity of acid, and once more precipitated. When the thorium is adequately purified, it is converted into thorium carbonate or hydroxide and dissolved in nitric acid. The solution is afterwards evaporated until thorium nitrate ( $Th(NO_3)_4 \cdot 4H_2O$ ) has crystallised out. Thorium nitrate is the principal commercial product. The element is not obtained in the pure form because it so readily combines with other elements at the temperature employed in its preparation. The purest metal so far obtained is made by heating the chloride, which is first purified by being sublimed in hydrogen, with metallic sodium in exhausted glass tubes. The product contains about 3% oxide.

The much-increased purchasing price of certain

chemicals, and in particular oxalic acid, used in one extraction process, has necessitated many changes in the methods designed for monazite sand, but these have been kept strictly secret. The refining of monazite produces as a by-product a radio-active product of thorium known as mesotherium.

Thorium is mainly employed in the manufacture of incandescent gas mantles, because, being an extremely poor conductor of heat, it can be brought to a high temperature. Gas mantles were first made in 1893 by Welsbach, who used a mixture comprising 98–99% thorium oxide, together with 1–2% cerium oxide. This mixture produces a brilliant light with the greatest possible luminosity. The method adopted is to dip the mantle, when made, and thoroughly dried, into a solution of the nitrates of thorium and cerium, comprising 99% thorium salt and 1% cerium. Those parts of the mantle likely to meet severe strains are treated with a thorium solution much richer in calcium, aluminium, or magnesium salts.

Cerium, the other rare element extracted from monazite, is prepared by electrolytic methods. The fused chlorides are subjected to electrolysis, small percentages of sodium or potassium chloride being usually added. The cathode is iron, and the anode, graphite. Because cerium burns readily in air with a brilliant flame, it is employed as a constituent of the pyrophoric alloy used in lighters. This application does not call for perfectly pure cerium, and in actual practice a mixture of the cerite metals is employed. By itself this would be too soft, and for this reason it is alloyed with a hard metal—e.g., auer metal, containing 35% of iron. Several of these mixtures have been the subject of patents for application to lighters. Similar alloys are also being employed on shells as tracer, to indicate the path.

Cerium has sometimes been proposed as an alloying element in steel, and at one time there was something of a ramp in these so-called cerium steels, which, however, proved to have no great superiority over less costly steels fulfilling identical purposes.

The extraction of cerium from monazite is achieved by mechanically purifying the mineral as far as it can be powdered and digested with concentrated sulphuric acid. All but a modicum of the surplus acid is removed, the residue being extracted with water. The filtrate, appropriately concentrated, is neutralised in order to cause precipitation of the phosphates. The phosphatic precipitation is then dissolved in hydrochloric acid, and this solution precipitated with oxalic acid.

The mixed oxalates are heated with sodium carbonate, which dissolves the thorium and precipitates the other rare metals as double carbonates. The carbonates are dissolved in hydrochloric acid and sodium sulphate is added, thus precipitating double sulphates. These double sulphates are boiled with strong sodium hydroxide, diluted, and filtered. The precipitate of the hydroxides is washed, dissolved in nitric acid, the reaction is adjusted, potassium bromate is added to oxidise the cerium, and the solution is then boiled with the addition of a quantity of marble in order to maintain only a neutral reaction. This causes the precipitation of a basic ceric nitrate. This is not pure, and to ensure purification the final stage must be repeated. From this the cerium compounds can be prepared.

Metallic cerium cannot be produced by electrolysis of the fused salts, except as a very fine powder. It cannot be obtained by reducing the oxide by carbon, as a carbide

forms, even when excess oxide is present. It is, however, possible to form copper-cerium alloys by adding CuO, which precludes formation of the carbide. Waste material from the gas-mantle industry can be employed for preparing metallic cerium. The oxides are dissolved in hydrochloric acid, with an excess of oxides. Sodium and phosphorus compounds are removed with barium chloride and iron, manganese and chromium by ceric oxide. The solution is then evaporated. After evaporation, fusion is carried out in cast-iron vessels high in carbon and silicon, and the fused salt boiled for 20 mins. The mixture is afterwards transferred to the electrolytic cell and electrolysed at 850° C. with an anode current density of 6–7 amp. per sq. in. for graphite and 5·5 amp. for carbon. About 7–12 volts pressure is employed.

### Rivet Sorting Machine

THE sorting of aircraft rivets is now being done almost eight times as quickly by a new machine developed by the Short complex of aircraft companies. The progressive grading of rivets is controlled by the size and form of screens carried on a number of trays worked electrically. They are first sorted according to diameter and placed on a coarse screen which passes all but the largest sizes. Those which pass are placed in a second tray, which retains the next largest size, and so on with the third tray. Rivets of the same diameter are then separated according to their type of head. An ingenious arrangement of slots and apertures in a special screen traps the round-headed rivets and passes the rivets with countersunk heads. The final operation collects the rivets according to length by adjusting a plate to hold those which are too long.

### Electrodepositors' Technical Society

A MEETING of the above Society will be held at the Northampton Polytechnic, Clerkenwell, E.C. 1, on June 21, 1943, at 5·30 p.m., at which a paper will be read by David D. Howat, B.Sc., Ph.D., F.I.C., on "Some Applications of Chromium Plating in Ordnance Manufacture." The author will discuss the high wear resistance and low frictional properties of chromium plating, and the application of these properties in a number of ways in ordnance manufacture—in the salvage of gun parts, in plug and ring gauges, in lathe centres, and in punches and dies. Particular attention will be directed to a new application in profile copy plate milling which has been developed with some interesting results. The life of the profile copy plates has been increased, a saving in expensive steel has been effected, and the manufacture of the finished components simplified.

### New Council

The following nominations for the new Council have been unanimously approved :—President, Dr. J. R. I. Hepburn; vice-presidents, Dr. G. E. Gardam and Dr. S. Wernick; hon. treasurer, Mr. F. L. James; hon. secretary, Dr. S. Wernick; asst. secretary, Miss L. Moore; immediate past president, Dr. H. J. T. Ellingham; chairman of Midland Centre, Mr. E. A. Ollard; hon. secretary of Midland Centre, Mr. H. J. Bache; Council: Messrs. H. Cann, A. W. Hothersall, J. Kronsbein, and J. W. Perring.

# The Gas-cutting Process and its Effects on Steel

By T. J. Palmer, A.M.Inst.W.

*The use of the oxygen-cutting process as a rapid and economical means of shaping metal is well known, and it is contributing to increased production in the present emergency, but ignorance or prejudice still prevail which hinder its fuller use. In this survey of the process general requirements are discussed, and attention is especially directed to some metallurgical aspects. It is shown that the process has no detrimental effect on the usual range of mild steels. The physical change in the metal adjacent to the cut edge is a change in structure with a slight carbon increase on the cut surface.*

THERE is nothing new in oxygen cutting, and the medley of uses to which the process has been adapted since its first appearance early in the present century are common knowledge. Its unique position as a rapid and economical means of shaping metal is indicated by the increasing number and diversity of applications in the field of modern production engineering, and the fact that other and more orthodox methods are less versatile and more expensive by comparison fully justifies the important place the cutting torch now occupies alongside the major shaping tools of the engineering industry. In the present arms drive it is indispensable.

Yet it is probably true to say oxygen cutting is not receiving the attention it merits and due, in certain instances, to ignorance, and in others prejudice, barriers still exist which hinder its use for operations where economic benefits would undoubtedly be realised. For instance, one occasionally hears from engineers' remarks to the effect that oxygen-cut edges are "burned up," with all the nature taken out of the adjacent metal; that it is not possible to machine such edges; or that, anyway, the cutting torch is only a rough tool capable of producing ugly and inaccurate cuts. Utterances like these are, of course, far removed from the facts, and it is hoped this survey of oxygen cutting and its effects will not only place the process in true perspective, but that as a result of refreshing our minds with the many variables involved a higher and more economical standard of workmanship will be demanded and maintained during these times when full operating efficiency, and the maximum conservation of oxygen are of such vital importance.

## General Requirements

Basic requirements for clean cutting with the oxygen torch are only completely fulfilled by very few commercial metals, the most important of which is iron, and it is fortunate that the basis metal of our present-day industry should come within this category. Iron and steel are, in fact, the only materials cut by this method on any extensive scale. As might be expected, elements and impurities associated with ferrous metals, which are not themselves amenable to cutting, or are difficult to cut, exert an important influence, and account for some irons and steels being more easily cut than others. Elements tending to oppose flame propagation in oxygen cutting include chromium, tungsten, silicon, aluminium, cobalt, and carbon (especially graphitic carbon). Taken individually, most of these elements, as present in minor

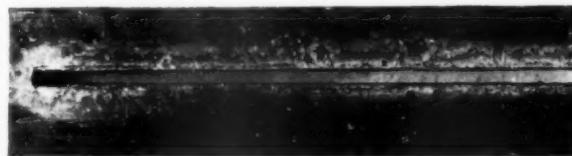
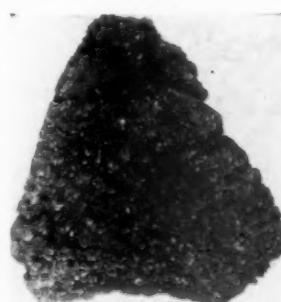


Fig. 1.—Oxygen cut in steel plate.

amounts, do not materially affect cutting, but are considerably influenced by the presence of others included in the iron or steel analysis. It is thus fairly evident that, apart from other considerations, the majority of cast irons and the more highly alloyed steels do not come under the heading of those materials which can be regarded as easily cut with the gas torch.

The action of cutting is simple enough. The edge of the metal is flame heated to about 875° C. and a stream of high-pressure oxygen then directed upon it. Combustion is initiated and spreads through the section until penetration is effected. During the reaction in which iron is converted to fluid iron oxide ( $3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4$ ) sufficient heat is developed to raise each neighbouring particle of metal to its ignition temperature—thus maintaining combustion. Movement along the plate of applied heat and oxygen through suitable mechanism—the cutting torch—permits the development of a clean, narrow cut (Fig. 1). Because of thermal losses during cutting, the heating flame hovers over the point of cutting throughout the operation. The products of the cutting reaction form, when cold, a solid non-metallic-like substance known as the slag (Fig. 2). It is composed of small particles of unoxidised iron (up to 30%) embedded in a mass of iron oxide.

Fig. 2.—Slag from the cutting reaction.



The actual cutting torch, which is, in effect, merely a modified arrangement of an ordinary welding torch, provides a flame for heating (e.g., oxy-acetylene, oxy-hydrogen, oxy-coal gas) and a stream or jet of oxygen for cutting. Oxygen is discharged eithe along the

axis of the heating flame, as in the concentric nozzle torch, or immediately behind the flame, as with certain older and less versatile types. The torch is moved over the work surface either by hand, as in hand-cutting, or mechanically, as in machine cutting. In some cases it is not practicable to use a machine, in which case the work

Fig. 3.—Good hand-made gas cut.

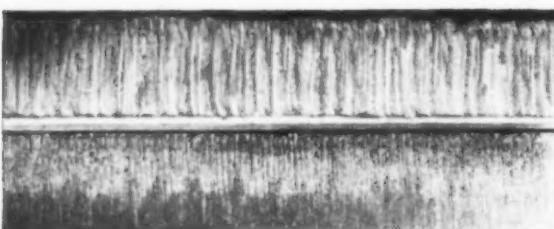


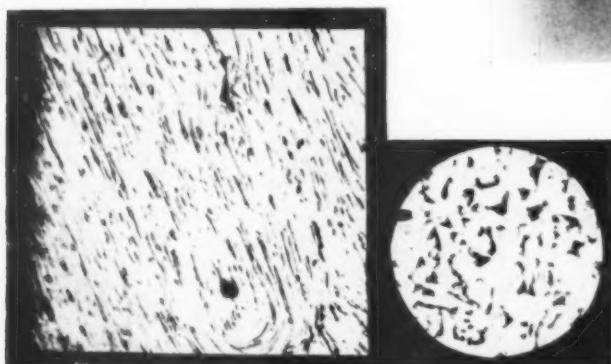
Fig. 4.—Good gas cut made with oxygen cutting machine.

is carried out freehand. Adjustable guides help to steady the torch and to maintain the nozzles at a fixed distance from the work. Use is made of straight edges, metal templets, etc., as desired. Cutting by hand requires a certain amount of skill, but, with practice, operators become fairly proficient and provided the shapes cut are not required to be too precise, thoroughly satisfactory work is possible. Because uniformity of movement and absolute steadiness of torch are of such fundamental importance in the delicate action of oxygen cutting, a far higher degree of precision is attainable in machine cutting than is possible with hand-cutting. A comparison of Figs. 3 and 4 are of interest in this connection

#### Machine Cutting

Thus, in machine cutting the torch forms a component part of the machine and is mechanically traversed over the work-piece—the desired shape generally being produced automatically. Modern oxygen-cutting machines are extremely versatile. They range in size from large stationary units of universal type, used principally for shape-cutting, to smaller, portable types designed to

Fig. 5.—Edge of sheared specimen showing distortion of constituents (ferrite and pearlite), and the base of a crack. For the purpose of comparison the unaffected structure is shown on the right.  $\times 75$ .



perform certain special tasks, such as cutting up billets, bars, tubes, rails, etc., or for cutting straight lines, curves, circles, discs, etc., with either square or bevelled edges. For shape-cutting, which constitutes the most important present-day application of oxygen machine cutting, ingenious tracing devices, fitted to the machine, guide the torch, which, in turn, accurately duplicates the most complex templet shapes, or produces work conforming directly to the details of a drawing.

Oxygen machine-cut edges are truly square, of even contour, and sufficiently smooth as to be easily comparable to those produced by sawing. They are infinitely superior to edges which have been sheared. (See Fig. 5.) Mechanical tests (tensile, bend, notch impact) performed on oxygen machine-cut low carbon, unalloyed steels show that the material is not adversely affected in cutting, since results obtained have been found equal to, and in some cases superior to those obtained on machined specimens.

#### Stack Cutting

Where a number of parts identical in shape are required to be cut from the same class of material the plate blanks are often placed in a stack and cut *en bloc*. Under suitable conditions this method of economically and accurately mass producing steel shapes is becoming increasingly used and has the advantage of being quicker than ordinary machine cutting. There are certain objections and limitations to the use of stack-cutting, however. Unless good surface contact between individual plates is assured the cutting operation will be interrupted and a large part of the stack probably scrapped. Since few unmachined plates are truly flat, some method of clamping them together is necessary in order to promote metallic continuity in the stack. For thin metal, suitably arranged "C" or "U" clamps are satisfactory. With more rigid material conditions of clamping become less easy, and, although correspondingly heavier clamps of a similar type may be used, it is frequently necessary to adopt different methods. Prior compression of the stack under a heavy press is often advisable in order to expel large air gaps. It is not uncommon to bolt, rivet or edge-weld the stack plates whilst under compression and then to transfer the whole to the cutting machine table. In all cases, care should be taken to assemble the stack

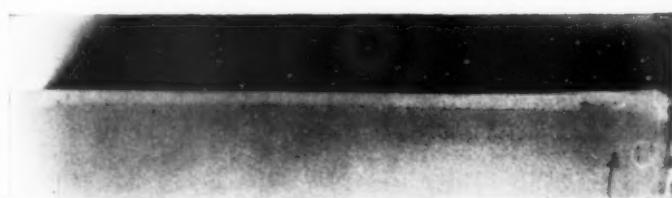


Fig. 6.—Macrograph of gas-cut edge in a 4-in. low-carbon steel billet, showing heat-affected zone. (Slightly reduced.)

with each plate reasonably free from dirt, oil, paint, rust or scale and with the leading edges in correct alignment.

Quite thick stacks can be cut, but, in order that full advantage is taken of the economies of stack-cutting, it is usual to limit the overall thickness to about 6 in. or even less, and the thickness of individual plates to about  $\frac{1}{2}$  in. A

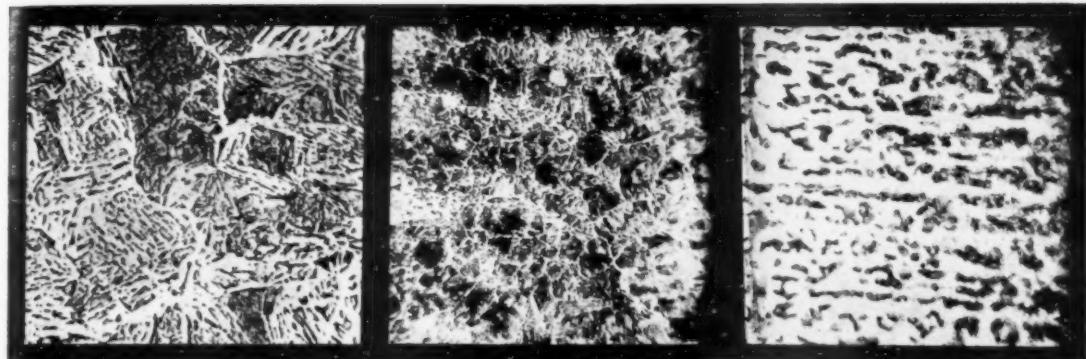


Fig. 7.—Gas-cut edge in 0.1% carbon steel. The structure produced by the heat of cutting is of a sorbitic nature.  $\times 100$ .

Fig. 8.—Gas cut in 0.22% carbon steel. The structure is sorbitic.  $\times 100$ .

Fig. 9.—Microstructure of a 12-in. mild-steel billet  $\frac{1}{4}$  in. from gas-cut edge. Considerable heat is developed in cutting thick material, and this large-grained, coarsely sorbitic structure of Widmanstätten type is typical of that observed in heavy cutting.  $\times 150$ .

heavy low-carbon steel "waster" plate is clamped to the top of the stack to ensure a rapid start, and also to prevent any damage to the uppermost plate. As compared with the cutting of solid metal of the same thickness, the working speed of the torch (other things being equal) should be slightly reduced for stack-cutting. Cutting nozzle size, oxygen pressure, and distance of torch from work, will naturally vary with stack thickness, but should be selected as for solid metal. As in all cutting operations, maximum economy in gas consumption is obtained from a suitable selection of the above in conjunction with an optimum working speed. Examination of stack-cut components should reveal sharp, square edges which will need a minimum of further machining.

#### Metallurgical Effects

Sufficient heat is evolved at the point of cutting to fuse the main reaction products and the neighbouring metal must, in consequence, undergo some local thermal disturbance. Micrographs suggest that temperatures upwards of  $1,000^{\circ}\text{C}$ . are attained in the metal immediately adjacent to the cut face, but that with correct cutting procedure the time during which the metal is held at such temperatures is short enough to limit noticeable structural changes to a zone of relatively small width. The total depth of alteration in structure as measured microscopically and taken at mid section rarely exceeds 0.125 in., with unalloyed low-carbon steel plates up to 6 in. thick. For 1-in. material it is less than half this amount. Even when cutting metal 20 in. thick the heat-affected zone does not generally exceed  $\frac{1}{16}$  in. High-carbon steels (up to 0.9% C.) and alloy steels are affected to a greater extent. The total depth altered is also influenced by the nature and size of the heating flame, by the surrounding metal mass, and to a lesser extent by the speed of torch travel. Due to the effects of the heating flame, the zone affected is greatest at the top, as is clearly seen from the macrograph reproduced in Fig. 6. Except for a slight increase at the base of the cut, the width remains fairly constant throughout the section. The former effect, which often varies considerably, is thought to be brought about by concentrations of liquid slag at that point.

In the absence of any auxiliary preheat, the cut face is bounded by cold metal, with the result that, according

to thickness of part, a fairly steep thermal gradient is established in the material immediately after cutting. Chilling occurs as heat is rapidly absorbed by the metal mass, and a set of conditions is produced analogous to those obtained in heating and quenching, or, for example, in the heat-affected zone of a single-run metal arc weld. Accordingly, composition of material and its susceptibility to hardening on sudden cooling become points of major importance, especially if the part is to be subsequently machined.

Carbon content of the steel is the most important single factor governing the degree of hardness produced near gas-cut edges, and its profound effect upon the cold-cutting of four plain carbon steels may be gathered from Figs. 7, 8, 10, and 11.

Metallographical changes in oxygen cutting mostly assume the form of those micro-constituents produced in ordinary heat-treatment operations, and with certain exceptions, any intense hardening is a result of the formation of martensite. From Figs. 7, 8, and 9 it is significant that with steels constituting by far the larger percentage of materials at present being cut with the gas torch—namely, unalloyed low-carbon steels—hardening in any important sense does not occur. The presence of a sorbitic type of micro-structure in the zone affected by heat accounts for an increase in hardness and toughness, as compared with the unaffected parent metal, but the increase is only small, and there should be no difficulty whatever in machining such steels after gas-cutting. Increasing the carbon content to 0.45% (Fig. 10) produces more important modifications and hardness is affected to a degree which interferes with machinability. The harder constituent troostite can be seen, and there is some martensite present. If steel containing 1% carbon is gas-cut, an edge structure almost entirely martensitic is produced (Fig. 11). The effect of this upon machinability is obvious.

In nearly all oxygen cuts, hardness in the heat-affected zone attains a maximum at the edge progressively decreasing as the unaffected material is approached. Actually, 0.3% represents about the limit of carbon which may be present if workable kerfs are

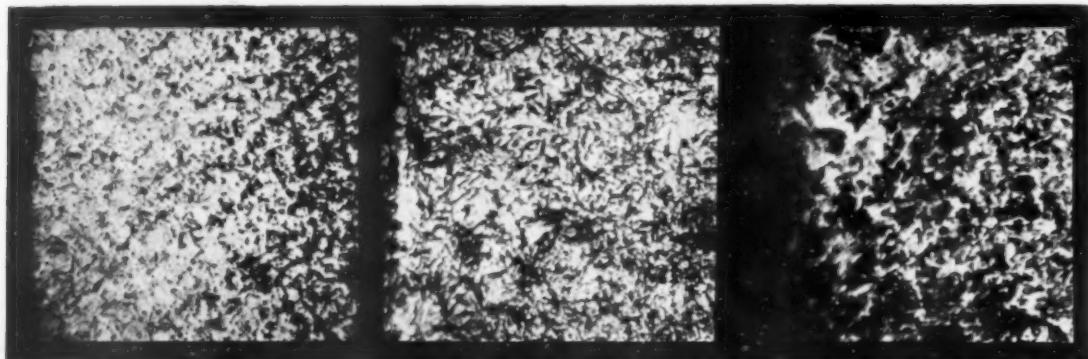


Fig. 10.—Gas-cut edge of a 0.45% carbon steel. The structure is of a troosto-martensitic nature gradually merging into that of a sorbitic type.  $\times 100$ .

Fig. 11.—Gas-cut edge of a 1% carbon steel showing needles of martensite.  $\times 500$ .

Fig. 12.—Showing excess carbide at the gas-cut edge of a 0.7% carbon steel.  $\times 500$ .

to be retained after cold-cutting. Above this amount it becomes necessary to either prevent the formation of, or break down, the harder constituents which tend to form. This applies only to plain carbon steels. The addition of alloying elements, particularly chromium, nickel and manganese, will definitely lower the above limit, and, in addition, may increase both width of the heat-affected zone and its hardness. It is as well to bear in mind that among the large and ever-growing range of "low-alloy" or "high-tensile" structural steels (which in most cases contain under 0.3% carbon) there are few which do not harden considerably after cold-cutting. If welding operations are to be carried out directly on the cut face, which, incidentally, is permissible, provided the requirements later laid down for a good cut are fulfilled, this hardness does not matter, because the heat of welding eliminates all structural alterations incident to cutting. Micrographs of welded, oxygen-cut plates reveal, in weld and transition zone, structures similar to those existing in the case of plates prepared by mechanical shaping methods.

In addition to alterations in microstructure, there are certain chemical changes during oxygen cutting. The most important is a migration of carbon (or of nickel) content to the edge. It is an established fact that this phenomenon does occur although as yet there appears to be no complete stabilisation of opinion between investigators as to exactly how this enrichment near the cut face is brought about. The subject might well form the nucleus of further research work. Carbon migration might account, at least in part, for the presence of a hard, white iron type of microstructure frequently observed at the extreme edge of certain steels which have been gas cut (Fig. 12).

#### Pre-heating and Annealing

Hard zones near the cut face produced as a result of cold-cutting the high carbon and alloy steels are objectionable for two reasons—firstly, machining with ordinary tools is made difficult, and secondly, cracks may be formed. Thus, additional preheat is frequently considered necessary when dealing with these steels. The effect of preheating before cutting is to limit the steepness of temperature gradient existing in the plates immediately after the cutting torch has passed by, to retard cooling speed through those critical temperature

ranges in which the harder and less ductile constituents are normally formed, and also to make the metal more receptive to the action of cutting. A furnace, or a surface-heating torch of the multi-flame variety can be used for the purpose. In the interests of smooth cutting it is desirable that a preheating temperature of  $650^{\circ}\text{C}$ . should not be exceeded—those usually employed ranging from  $300^{\circ}\text{C}$ . to  $500^{\circ}\text{C}$ . according to the type and thickness of material.

Unless homogeneity of physical structure is required, heating or annealing after cutting is usually considered unnecessary with steels that have been preheated prior to gas-cutting, since, unless the steel is fully air hardened, the kerf is generally left soft enough for most purposes. Metal which has hardened up as a consequence of cold-cutting can, of course, be annealed, and any hard formation would be broken down in the operation. The process would, in effect, more completely achieve the same end as preheating before cutting. Nevertheless, cooling stresses inevitably attend the cutting operation, and there is always the possibility of cracks being developed in the hardened zone.

In view of this, it might be wise to remember that prevention is better than cure, and to preheat before cutting because no amount of post-heating will heal cracks already formed.

(To be continued.)

#### Royal Aeronautical Society

On Friday, June 25, 1943, a discussion will take place before the above Society on "The Education and Training of Aeronautical Engineers." The meeting is arranged to be held in the Lecture Hall of the Institution of Mechanical Engineers, and will begin at 5.30 p.m. at Storey's Gate, S.W. 1.

The discussion is intended to cover every side of aeronautical engineering training, and will be opened by Sir Roy Fedden with an outline of training in America.

In view of the importance of providing for an adequate supply of trained engineers in industry, in research, and in the Royal Air Force, it is hoped that all those who have views on aeronautical education, whether members of the Society or not, will come along and express them. The Society will also welcome any written views.

# A Review of Basic Open-Hearth Steel Practice at an Australian Plant\*

By R. L. Knight

*In this the concluding part of this review, presented at the recent Annual Meeting of the Iron and Steel Institute, particular attention is directed to slag control in the production of semi-killed steels, phosphorised sheet bar, rimming steel and alloy, and forging steels. Rapid methods of analysis for lime, silica and iron oxide have been developed at this plant.*

## Slag Control

**I**N Australia, as in other countries, the purchaser has become more critical of the material he buys. Rapid expansion of industry here has contributed to this, and research for cheaper steels with properties comparable with the more expensive alloy steels is stimulated. The manufacture of repetition parts on automatic machines demands uniformity in feed. These considerations have placed on the steelmaker the onus of producing the required quality consistently from heat to heat. Closer tolerances in chemical analyses have to be met, and in some instances orders are endorsed for grain size, cleanliness, and other special requirements. Open-hearth operators have had to pay closer attention to quality and to establish practices to meet these requirements.

It is realised that our predecessors did endeavour to finish heats with "good slags," but generally the slags were high in lime for all grades of steel, frequently with unfortunate economical and metallurgical results. The technique of basic open-hearth operation has made great strides forward in the past 20 years, the most cogent stimulus having been derived from research work on slags and slag-metal reactions. To such work may be attributed much of the improved qualitative perspective in the furnacing of steel.

Slag control may be defined as the step in the process of steelmaking that is directed to the adjustment of the slag composition to the best advantage. It gives the metal the desired condition at tapping, and, associated with suitable deoxidation and temperature control, produces steel of the required composition, type and uniformity in the mould at the lowest cost.

A review of contemporary literature on this subject reveals that there are nearly as many practical systems of control as plants, but it is obvious that any system, to be successful, must be developed compatibly with local conditions. Consistent high quality is the primary consideration, and if this can be obtained with economies, however small, the interest of everyone concerned is assured. The system should be as simple as possible, reduced to terms easily understood by practical furnace-men, and policed by metallurgical observers.

The practice of slag control at Kembla dates from 1932, since when investigation has been continuous. Many theories and methods were tested and rejected before finally the practice was adopted of depending entirely on the analysts for information on the slag and metal in the furnace. There are two chemists on the floor for each shift, a senior man on steel analyses, and one junior on slags. Lime results are obtained within

30 mins. of spooning the slag from the bath, silica within 35 mins., and iron protoxide or total iron in 15 mins.

With the available raw materials the phosphorus pentoxide carried in the slag with a 9% slag volume averages 1%; hence it is possible to regulate the lime-silica ratio within wide limits without danger of re-phosphorising the metal. Therefore, the slag oxidation is able to be kept low and the residual manganese high, with valuable savings in ferro-manganese consumption. Producing structural grades with 0·4-0·6% of manganese, the plant has made 7,000 tons of steel in consecutive heats without adding ferro-manganese to the bath or ladle. On all grades the plant has worked for a full month using an average of 1·5 lb. of 78% ferro-manganese per ton of ingot, notwithstanding that some of the heats contained 1·7% of manganese.

Figs. 8 and 9 indicate the relationship between slag basicity, residual manganese and total slag oxidation.

The introduction of a 1,200-ton hot-metal mixer in 1940 improved operations further. From the analyses of mixer samples the melters are able to charge the furnaces more accurately to melt within the carbon range specified. Limestone is saved and "bottom" heats are fewer. The smoother, steadier working of the furnaces facilitates the metallurgical control.

## Production of Semi-Killed Steels

The analysis range of semi-killed steels is as follows :—

Carbon,	Phosphorus,	Manganese,	Silicon,	Sulphur,
0·1-0·35	0·06 max.	0·1-0·8	0·3 max.	0·06 max.

These heats are poured into wide-end-down 25-in. × 21-in. corrugated moulds with typical convex ingot tops. Furnace charges for such heats are :—

	160-ton Heats.	230-ton Heats.
Mill scrap .....	25	35
Hot metal (Si 0·9%) .....	115	195
Manganiferous ore .....	12	46
Limestone .....	8	11

When the slag is made up, the bath is sampled for metal and slag. Carbon, manganese and phosphorus are estimated in the metal, and lime, silica and iron protoxide in the slag. The melter proceeds to work the heat according to plan. Manganiferous lump ore is fed to reduce the carbon, and sand is added to reduce the basicity, if necessary. The schedule for the sand addition, for instance, for the 160-ton heat is as follows :—

$\text{SiO}_2$ in slag % ..	10	11	12	13	14	15	16	17
Sand required in lb. ..	2,100	1,900	1,500	1,200	900	800	600	300

If the slag is too siliceous, limestone chips are charged.

\* Continued from May issue, page 46.

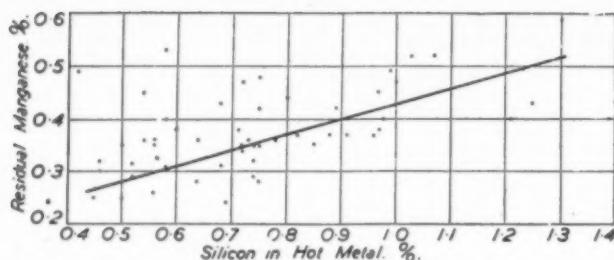


Fig. 8.—Silicon content of the hot metal plotted against the residual manganese.

Kembla experiments confirm the finding of Earnshaw Cook,<sup>1</sup> that carbon is necessary for the sand to be effectual in reducing the proportion of iron protoxide; the bath carbon must exceed 0.3% when the sand is added. The diminution in the iron-oxide concentration, following the addition of sand, is out of all proportion to the dilution. It may be assumed that a partial replacement of iron oxide by silica occurs in lime/iron-oxide compounds, allowing some iron oxide to migrate to the metal and effect a slight oxidation of carbon. At the same time there is a reversion of manganese, to an extent governed by its degree of concentration in the slag and metal, and the iron oxide content of the slag. The examples given in Table VIII indicate the practical application of controlled lime-silica ratios for semi-killed steels with up to 0.35% carbon.

Ferro-silicon additions are made according to the proportion of iron protoxide in the finishing slag.

Kembla practice for low- and medium-carbon semi-killed heats is along the following lines:—

(a) The amount of run-off slag is carefully watched, and the take-off is constant from heat to heat for equal charge compositions and metal analyses.

(b) Slag volumes are kept as low as is consistent with effective coverage.

(c) Finishing slags are run to a lime-silica ratio of 2.0 or 2.2 to 1.

This practice improves the furnace yield by reducing the iron losses in the slag and keeps the residual man-

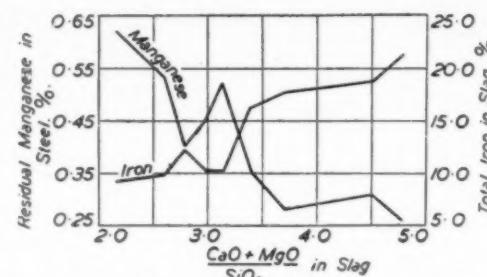


Fig. 9.—Relationship of the slag basicity to the residual manganese and to the total iron in the slag.

ganese high, with savings in alloy consumption. For any given concentration of manganese in the charge, the residual manganese will vary inversely with the basicity of the finishing slag. The average composition of the finishing slags from 50 semi-killed heats was:—

$\text{SiO}_2$ , %	$\text{FeO}$ , %	$\text{Fe}_2\text{O}_3$ , %	$\text{Al}_2\text{O}_3$ , %	$\text{MnO}$ , %	$\text{CaO}$ , %	$\text{MgO}$ , %	$\text{P}_2\text{O}_5$ , %
17.7	7.7	4.0	4.3	23.3	35.1	6.8	1.1

Critical examination of the figures for three years of production proves that sand, intelligently used, does no damage to banks and bottoms. Dry sand added to the basic furnace becomes dissolved in the slag within a few minutes. It has no tendency to agglomerate and move to the banks. Sand should be regarded as a necessary basic open-hearth flux, and the controlled use of it recognised as a valuable aid in the production of basic steel.

Several hundred thousand tons of steel have been made at Kembla carrying sufficient residual manganese to be independent of ferro-manganese additions. Such steel is of consistently high quality, its physical tests are excellent, and it rolls well with a minimum of reconditioning.

#### Production of Phosphorised Sheet Bar

A further interesting example of slag control is the production of sheet-bar ingots to the specification:—

Carbon, %	Phosphorus, %	Manganese, %	Silicon, %	Sulphur, %
0.14 max.	0.06-0.09	0.45 max.	0.10 max.	0.06 max.

TABLE VIII.—APPLICATION OF CONTROLLED LIME-SILICA RATIOS TO SEMI-KILLED STEELS.

Heat No.:	E 136,			B 140,			D 278,		
Charge:									
Mill scrap .....	40 tons			10 tons			30 tons		
Hot metal .....	110 tons			111 tons			120 tons		
Limestone .....	7 tons			7 tons			6 tons		
Analysis of hot metal:									
Silicon .....	0.9%			0.9%			0.9%		
Manganese .....	2.1%			2.1%			1.9%		
Run-off slag .....	1 pot			1 pot			1 pot		
Bath:									
Time, Addition, C, Mn, FeO,									
9-10      —      0.38      0.43      9.6									
9-25      Sand 0.1 ton      —      —      —	12.55	Ore 0.9 ton	0.85	—	14.0	11.15	Ore 1.7 ton	1.00	0.38
9-25      Ore 0.8 ton      —      —      —	14.42	Sand 0.4 ton	0.43	0.31	—	11.57	Sand 0.9 ton	0.46	0.12
10-10      —      0.27      0.55      —	—	—	2.15	—	—	12.08	Ore 0.4 ton	0.45	0.43
10-22      —      0.20      0.56      —	—	—	2.28	—	—	12.24	—	0.36	0.48
Ladle additions:									
Ferro-silicon (70%) .....	0.22 ton			0.23 ton			0.20 ton		
Ferro-manganese (78%) .....	Nil			0.25 ton			Nil		
Coke .....	0.27 ton			0.18 ton			0.14 ton		
Ladle analysis:									
Carbon .....	0.28%			0.30%			0.25%		
Phosphorus .....	0.018%			0.015%			0.021%		
Manganese .....	0.55%			0.51%			0.55%		
Silicon .....	0.08%			0.10%			0.09%		
Sulphur .....	0.028%			0.038%			0.040%		
Ingot tops .....	Convex			Convex			Convex		
Aluminium per ton .....	0.25 oz.			0.15 oz.			Nil		

TABLE IX.—LOGS OF TYPICAL HEATS FOR PHOSPHORISED SHEET BAR.

Heat No.:	G 138-9.						G 140-1.					
Charge:												
Scrap .....	35 tons						35 tons					
Hot metal .....	205 tons						205 tons					
Ore .....	48 tons						44 tons					
Limestone .....	5 tons						5·1 tons					
Phosphate rock .....	2·3 tons						2·3 tons					
Hot-metal analysis:												
Silicon .....	1·1%						0·4%					
Manganese .....	2·4%						2·2%					
Run-off slag .....	2 pots						1½ pots					
Bath :												
Time.	Sand.	C,	Mn,	P,	FeO,	SiO <sub>2</sub> ,	Time.	Sand.	C,	Mn,	P,	FeO,
9·15	0·45 ton	—	—	—	—	—	11·15	0·40 ton	0·18	0·42	0·045	—
10·10	—	0·40	—	0·08	8·5	20·2	11·30	—	—	—	—	9·9
11·30	—	—	0·10	0·43	0·07	—	12·04	—	0·08	0·17	0·07	—
11·40	—	—	—	—	—	8·7	12·22	—	—	0·13	—	—
11·55	—	—	—	0·43	—	—	12·35	—	—	—	—	10·3
12·05	—	—	—	—	—	Tap	—	—	—	—	—	—
Ladle addition :												
Ferro-silicon (76%) .....	No. 1, 0·17 ton						No. 1, 0·18 ton					
Ladle analysis :							No. 2, 0·18 ton					
Carbon .....	0·08%						0·08%					
Phosphorus .....	0·08%						0·09%					
Manganese .....	0·35%						0·37%					
Silicon .....	0·05%						0·05%					
Sulphur .....	0·023%						0·024%					

Formerly this steel was made by furnacing for a low-carbon heat and adding ferro-phosphorus to the ladle. The method has been superseded by controlling the reversion of phosphorus to the bath metal from a finishing slag of suitable composition. Some of the limestone burden is replaced by phosphate rock, and the slag basicity is adjusted in the finishing stages of the heat. The slag oxidation is kept low and the bath is kept hot. On charging 20 lb. of rock per ton of ingot the finishing slag will contain about 3% of phosphorus pentoxide, a proportion suitable for easy manipulation and control. Logs of typical heats are shown in Table IX, and slag compositions in Table X.

This practice was introduced as a war-time expediency and has given satisfactory results. Quick and accurate control is essential to success. Furnacemen soon become expert in the adjustment of conditions.

#### Production of Rimming Steel

Practically the whole output of the fully open type of steel is rolled into high-finish deep-drawing automobile sheets. Open-hearth operators are aware of the close attention and co-operation required for the production of high-grade ingots for such requirements. Much of the deep-drawing steel made abroad is produced from 40% pig-iron charges. In some plants it is considered that deep-drawing grades cannot be made satisfactory from high hot-metal charges. When this grade of steel came into demand at Kembla in 1937 it was necessary to avoid interference with the existing open-hearth and blast-furnace routine. A practice thus became established with around 70% hot-metal charges, from which rimming ingots of first quality with thick skins and a high degree of cleanliness are obtained.

Typical logs of rimming steel heats are given in Table XI.

The charge ore is basic, containing 2% of manganese. The logs show residual manganese somewhat higher than in oversea plants. Here it varies between 0·17% and 0·25%, and it is found that, with other conditions satisfactory, up to 0·25% has no adverse effect on quality. Deoxidation charts made available to meltters show the amount of aluminium for the ladle, based on

TABLE X.—SLAGS OF SHEET-BAR HEATS COMPOSITE SAMPLES

Number of Heats, %	24	35	11	15
SiO <sub>2</sub> .....	17·2	16·6	18·3	18·3
FeO .....	12·0	13·2	12·1	9·5
Fe <sub>2</sub> O <sub>3</sub> .....	4·4	3·1	3·7	3·7
Al <sub>2</sub> O <sub>3</sub> .....	5·4	4·1	4·2	3·3
MnO .....	24·3	26·8	27·7	28·3
CaO .....	27·3	26·8	25·0	28·2
MgO .....	6·0	6·0	7·0	5·7
P <sub>2</sub> O <sub>5</sub> .....	3·4	2·0	2·0	2·8

the total iron in the slag and the residual manganese in the metal. The amount varies from 60 lb. with 28% of iron and 0·15% of manganese to 5 lb. with 17% and 0·26%, respectively. It will be observed that the total iron figure is used as a measure of slag oxidation. From the FeO figure erratic results may occur with high-lime slags on heats tapped below 0·10% of carbon. In such slags there is a wide variation in the Fe<sub>2</sub>O<sub>3</sub> present, and more consistent results have been obtained by using the total-iron results.

When making rimming heats it is desirable to keep them hot right through. The melting-down carbon should be such that the furnace will take from 1 to 3 tons of ore in order to maintain an active bath boil right up to the tapping point. This is essential to the production of ingots free from skin blow-holes. A further requirement when running high-metal heats is to take sufficient and constant quantities of flush slag. If this aspect is neglected much furnace time will be lost in reconditioning the finishing slags. No effort should be made to economise in limestone, which, it will be noted, amounts to 210 lb. per ton of ingots, for such procedure would be more than offset by loss of operating time in waiting for the iron oxide to build up in the slag. Slag volumes average 15%.

Should the slag chemist report a suitable basicity, the heat is oreed down in the usual way. Oreing is complete at least 1 hour before tapping. Should the slag come up more siliceous than is desired, sufficient quantities of dry limestone chips are charged. Burned lime is expensive and difficult to store without acquiring moisture. Partly hydrated lime is considered to be a potential source of hydrogen and a cause of thin-skinned ingots.

TABLE XI.—LOGS OF TYPICAL HEATS OF RIMMING STEEL.

Specification:	Carbon, %	Phosphorus, %	Manganese, %	Silicon, %	Sulphur, %	Copper, %
0.08-0.10	0.04	0.32	0.40	Residual	0.035 max.	0.10 max.
Heat No.:	C 73,	D 43,	F 249,			
Hot metal .....	120 tons	121 tons	124 tons			
Scrap .....	30 tons	30 tons	27 tons			
Limestone .....	15 tons	15 tons	15 tons			
Ore .....	27 tons	29 tons	24 tons			
Total metallic .....	168 tons	170 tons	167 tons			
Previous heat tapped .....	5.23 p.m.	10.30 a.m.	3.37 p.m.			
Commenced to charge .....	6.50 p.m.	10.50 a.m.	4.42 p.m.			
Melted .....	—	9.00 p.m.	2.15 p.m.			
Tapped .....	8.20 a.m.	12.22 a.m.	3.38 a.m.			
Run-off slag .....	1 full pot	1 full pot	1 full pot			
Bath additions:						
Ore .....	1.0 tons	5.0 tons	1.0 ton			
Limestone .....	Nil	2.5 tons	Nil			
Ladle additions:						
Ferro-manganese (78% ..)	0.4 lb.	0.35 lb.	0.35 lb.			
Coke .....	Nil	0.09 lb.	0.07 lb.			
Aluminium .....	0.013 lb.	0.007 lb.	0.013 lb.			
Analyses:						
Hot metal:						
Silicon .....	0.8%	1.3%	0.7%			
Manganese .....	2.9%	2.4%	2.6%			
Bath at melt:						
Carbon .....	1.0%	1.5%	0.27%			
Manganese .....	0.27%	0.52%	0.26%			
Phosphorus .....	0.025%	0.025%	0.020%			
Sulphur .....	—	0.028%	—			
Bath tapping:						
Carbon .....	0.07%	0.05%	0.06%			
Manganese .....	0.22%	0.19%	0.21%			
Phosphorus .....	0.01%	0.01%	0.01%			
Slag:						
SiO <sub>2</sub> .....	11.2%	12.0%	12.0%			
CaO .....	10.4%	37.6%	36.1%			
Total iron .....	22.5%	19.6%	22.5%			
Ladle:						
Carbon .....	0.08%	0.09%	0.09%			
Manganese .....	0.10%	0.32%	0.34%			
Silicon .....	0.008%	0.009%	0.007%			
Sulphur .....	0.021%	0.029%	0.020%			
Phosphorus .....	0.010%	0.010%	0.008%			
Copper .....	Nil	Nil	Nil			
Pouring:						
Nozzle, Imp. clay .....	1/2 in.	1/2 in.	1/2 in.			
Stopper .....	Graphite	Graphite	Graphite			
Temperature .....	Good	Good	Good			
Aluminium per mould .....	3 oz.	4 oz.	2 oz.			
Ingot weight .....	3-4 tons	3-4 tons	3-4 tons			
Total weight .....	156-1 tons	156-1 tons	159-3 tons			
Stoppers .....	Clean	Clean	Both slight			
Rimming action .....	Brisk, falling, Rim 1-2 in.	Active, falling, Rim 2 in.	Even rim, Fairly brisk, 8 ingots			
Rim 1-2 in.	Clean, Good surface.	Good surface.	slightly splashed,			
Clean, Good surface.	Nil	Nil	0.67 tons			
Yes	Yes	Yes	Yes			
Ladle skull .....						
Cardboard used .....						

All slags are not fully analysed as a matter of routine, for the control system supplies the necessary information from heat to heat. Composite samples of slag are made up periodically comprising those from 15-20 heats. Some typical single slags are shown in Table XII.

Rimming steel is tapped hotter than semi-killed steel of similar carbon range. The melter's practical methods are checked by the metallurgical observer with a disappearing filament optical pyrometer. The first helper slags a 4-in. dia. spoon and dips deeply for metal, withdrawing the spoon to just inside the door spy-hole. By tilting the spoon the observer is able to get a quick "shot" at the bare metal, and with practice becomes adept.

TABLE XII.—TYPICAL RIMMING-STEEL SLAGS

Heat No.:	B 127,	D 380,	A 26,	A 32,	B 211,	B 213,	E 706,
SiO <sub>2</sub> .....	9.3	10.3	9.6	11.5	9.0	12.0	10.7
FeO .....	26.7	14.2	—	—	—	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	7.7	14.7	—	—	—	—	—
Al <sub>2</sub> O <sub>3</sub> .....	1.2	3.7	—	—	—	—	—
CaO .....	0.9	0.9	—	—	—	—	—
MnO .....	10.5	11.5	—	—	—	—	—
CaO .....	31.5	33.9	35.2	37.1	31.3	40.2	45.0
MgO .....	9.2	10.8	—	—	—	—	—
Total iron, % .....	26.2	21.3	26.3	21.1	28.2	23.7	21.3
CaO/SiO <sub>2</sub> ratio .....	3.4	3.3	3.7	3.2	3.8	3.3	4.2

The objective is to pour ingots that rim actively in the moulds with 1-2 in. of fall. Such ingots show 4 in. of rim depth on a 25-in. x 21-in. x 63-in. ingot. This gives the sheet-maker ample latitude in the subsequent processing. Aluminium in the pit is regarded as a corrective for slightly over-oxidised steel, but the condition of the metal from the furnace must be satisfactory.

### Production of Alloy and Forging Steels

Special steels in alloy and plain-carbon grades are made in the 160-ton furnaces. Written instructions are issued and obeyed. The same principles of slag control apply, and the lime/silica ratios vary between 2.5 and 2.7. Heats are slightly overcharged with lime, and small regular additions of sand are made in the early stages to correct the slag composition and inhibit the rise of FeO.

Heats are made with the lowest FeO content in the slag that is compatible with low-phosphorus in the metal, and FeO can usually be controlled to a "three-point spread." Special attention is paid to the rate of carbon diminution, and over-oreing is not permitted. Ore is seldom added within 2 hours before blocking and alloying, the last few points of carbon being shaken out with rabbles. In making expensive alloy grades, flush-slag practice is omitted in order to avoid possible variations and to recover alloy from the scrap. The grain-size is controlled entirely in the ladle. All alloys, except silicon, are added to the bath. These heats are held in the moulds for 2 hours before stripping and transferring to the soaking pit.

### High-Temperature Resistivity Measurements on Compressed Granular Refractory Materials

A QUICK, cheap method has been developed by Fetterley\* for the determination of the specific resistance of compressed granular refractory materials at temperatures up to 1,000°C. The leakage resistance of tubular heating elements insulated with periclase has been found to be proportional to the resistivity coefficient of the grain used for insulation. The theoretical derivation and method of calculation of this factor are given.

$$\text{The Joffé law, } R_s = Ae^{\frac{T}{T}} \text{ or } \log R_s = A + \frac{B}{T} \text{ has}$$

been verified for periclase in the range of 600° to 1,000°C. R<sub>s</sub> is the specific resistance; A and B are constants; T the absolute temperature; and e the exponential value 2.718.

Results of measurements on periclase of different degrees of purity are in general agreement with those obtained by Rochow<sup>1</sup> and by Heine.<sup>2</sup>

It has been shown that some additions to periclase, notably alumina, increase its resistivity to a very useful degree below 1,000°C, though the effect is probably opposite at very high temperatures. The presence of iron and boron has been shown to be especially harmful.

Periclase and especially alumina were found to show dielectric absorption effects. In the case of periclase containing alumina or spinel, the ratio of d.c. to a.c. resistance was found to be a function of the alumina content.

\* G. H. Fetterley, Electrochem. Soc., 1943, Preprint 83-2.

<sup>1</sup> E. G. Rochow, *J. Applied Phys.*, 9, 661 (1938).

<sup>2</sup> K. Heine, *Ber. deut. Keram. Ges.*, 19, 461-469 (1938).

# Tropenas Converter Practice

By E. C. Pigott

*For the production of steel castings the converter has many advantages. After considerable development of this steel-making process the Tropenas converter has become more generally applied in foundry practice. The author briefly reviews the development of this converter, and gives an account of its operation. Attention is especially directed to the need of scientific control to obtain the most satisfactory results.*

THE Tropenas converter, for which Alexander Tropenas was granted a patent, was introduced in 1891.<sup>1</sup> The main features, in comparison with previous designs, were surface-blowing, a deeper bath, conical bottom to keep the bath free from mechanical disturbance, and increased thermal economy, effected by means of an auxiliary row of tuyeres which minimised the proportion of carbon monoxide.<sup>2, 3, 4</sup> Formerly, it had been firmly held that an essential requirement of successful blowing was the production of a violent swirling action of the molten metal by directing the air upwards through the bath. The evolution of the small converter was marked by a gradual raising of the tuyeres from near the bottom of the vessel towards the surface of the bath. Finally, Tropenas arranged for the air to impinge upon the surface of the metal. In doing so he revolutionised small converter practice. His first plant, erected at Messrs. Edgar Allen's, of Sheffield,<sup>5</sup> was completed in 1892. The vessel had a capacity of 800 lb., but considerations of economy led to experiments with larger vessels, a capacity of 2 tons being found preferable. In 1896 Messrs. Edgar Allen had two vessels of this size, each averaging five blows in an average of two hours, and yielding up to 37 cwt. per blow. For deoxidising, ferro-silicon was used with ferro-manganese. It was claimed that the average tensile strength on 2-in. test-pieces was 30 tons, with 31% elongation and 47% reduction of area.

Two independent wind boxes were arranged about the vessel, each supplied through separate valves from the air main. The lower box contained 1½ in. × 2 in. tuyeres at the level of the bath, and those in the upper box, 4 in. to 7 in. higher, were tapered to ¾ in. The upper row, which served to raise the temperature considerably, was open for the duration of the carbon flame. Explaining the two rows of tuyeres, shown in his patent of 1891, Tropenas claimed a method of increasing the temperature within the converter by projecting air through tuyeres arranged at a sufficient height for causing combustion of the carbon monoxide and hydrogen evolved during operation. Actually, the second row was within a few years to be found unnecessary.<sup>6</sup> A blast of 3–4 lb. per sq. in. was used, according to the type of pig iron. The metal was recarburised with additional molten pig iron, accurately weighed.

The surface blowing gave higher temperatures and a superior quality of steel, the bath remaining quiet without the vigorous mixing of metal, slag and air involved in

other processes. The blown metal contained as much as 99·8% of iron, and was almost free from dissolved gases. The oxidation of iron proved somewhat greater than in the Bessemer process. The total blowing losses were 10–12½%. The molten charge contained 2·5–3·0% silicon, 0·5–1·25% manganese and 3·0–4·4% carbon. The blow lasted 15–20 mins. Silica bricks, cemented with sand and clay, were used for the lining, which was repaired between blows, and survived 125–150 operations. The tuyeres lasted 30–40 blows.

In 1898 a third 2-ton vessel was added to the Edgar Allen plant, which then provided all the metal required for the firm's steel castings, whilst 15 other concerns were operating over 30 Tropenas converters of 1–2 tons capacity. In 1900 the annual output from Tropenas converters exceeded 50,000 tons, the process having become the most extensively employed for steel castings.

In 1904 it was widely recognised that the depth of the bath must be kept within limits.<sup>7, 8</sup> Neither must the relative surface be too great. Experiments with charges smaller than 1 ton were carried out in the United States, but were again found impracticable. heat-absorption by the lining being too considerable. The efficiency of the 2-ton converter had improved and, temperatures were apt to be excessive, cold scrap being added to the ladle to prevent cracking of the castings.<sup>9</sup> The cupola coke-consumption required to give the necessary temperature was found to be 20% of the metal charged. The effect of the skill of the blower on the fusion losses was clearly appreciated, high blast pressures, rapid blowing, a high-silicon content or cold metal, each causing heavy losses. Average fusion losses were 11%, and cupola losses 7%. The profitable field for the small Bessemer was realised as being that of small castings. One operator recommended preheating with gas, a much cheaper fuel than silicon. Linings were found to suffer if the manganese content exceeded 0·5%.

By 1905 the small Bessemer had no rival for small foundries,<sup>10</sup> and its adaptability was rendering it a very useful adjunct to engineering work. The crucible process was very much too expensive, whilst open-hearth steel cooled too quickly, leaving heavy residues, besides failing to reach the intricate crevices in the moulds.<sup>11</sup> The lateral blast had been established as being more efficient than bottom-blowing. In 1906 Simonson<sup>12, 13, 14, 15</sup>

1 Abridgements of Patents, Class 72 (Brit. Patent No. 7625).

2 Iron Age, **57**, 1074; J.I.S.I., 1896, ii, 384.

3 Powell and Tropenas, J. Amer. Foundrymen's Assocn., **5**, 118–141; J.I.S.I., 1898, ii, 510.

4 Tropenas, J. Amer. Foundrymen's Assocn., **10**, 109–119; J.I.S.I., 1901, ii, 479.

5 A. Johansson. *Bihang till Jernkontorets Annaler*, 1902, 197; J.I.S.I., 1902, ii, 519.

6 Schmidt. *Eisen-Zeitung*, 1906, No. 1 and 2; J.I.S.I., 1906, 445.

7 N. Lilienberg. *Iron Trade Review*, Jan. 14, 1904, 37; J.I.S.I., 1904, i, 631.

8 N. Lilienberg. *Bihang till Jernkontorets Annaler*, 1904, 353–367; J.I.S.I., 1905, ii, 720.

9 Unckenbold. *Stahl und Eisen*, **23**, 1227; J.I.S.I., 1904, i, 632.

10 Operation of Tropenas Converter at Royal Arsenal, Woolwich, Engineering, **65**, 43; 1898, 491.

11 G. Weyland. *Revue Universelle des Mines*, **9**, 251–261; J.I.S.I., 1905, i, 707.

12 A. Simonson. *Iron Trade Review*, Oct. 18, 1906, 24; J.I.S.I., 1907, i, 500.

13 A. Simonson. *Iron Trade Review*, Nov. 15, 1906, 29; J.I.S.I., 1907, i, 500.

14 A. Simonson. *Foundry*, 29, Nos. 2 and 4; J.I.S.I., 1907, i, 500.

confirmed that the place of the Tropenas was in the manufacture of small and medium castings of a specially high grade of steel, sound and close-grained, the product being specially suitable for automobile parts, gears, valves, levers, turbine parts, gas engines and general machine work. He had found the Tropenas very useful as an annex to the open-hearth furnace, providing a balanced supply of metal for a wide range of castings. An analytical laboratory was realised to be essential. Simonson<sup>16</sup> enumerated casting requirements as follows : (i) Temperature, (ii) fluid metal, (iii) retention of fluidity long enough to be distributed in small ladles where necessary, (iv) regularity, (v) complete deoxidation, and (vi) compliance with specifications. Refining systems must be simple and inexpensive to install. Analysis of the pig iron used in the cupola charge should be 3·8-4·5% carbon, 0·5-2·0% manganese, 1·8-3·0% silicon, less than 0·05% of sulphur, and less than 0·06% of phosphorus. The greater the proportion of scrap used the higher should be the silicon content of the pig iron. The time taken from blowing to casting was 35-45 mins., and allowing 5 mins. for charging, the output was 1,000 lb. of steel every 45 mins.

The adaptability of the small converter had rendered it a useful adjunct to engineering works. About this time Tropenas introduced a drop bottom device consisting, as in cupolas, of two hinged parts closed by a bar. It provided rapid cooling, thus permitting patching on the following morning and blowing on successive days, instead of alternate days.

The Tropenas converter of to-day differs from the original in several respects. The upper row of tuyeres has been dispensed with, a shallower bath is provided for, and both top and bottom portions are detachable. Thus, it incorporates features introduced from other small types. The single row of tuyeres and the detachable bottom, both of which are now general, figure in the Stoughton, whilst the detachable upper portion is found in the Whiting. In fact, most converters have played a part in the evolution of the present design. Similarly, with practice—the exhaustive descriptions published by Tropenas himself were supplemented by Simonson, Stoughton and others. The addition of ferro-silicon during the blow in order to raise the temperature of the bath is derived from Walrand. The original shape and capacity of about 2 tons favoured by the inventor have been amply confirmed as the most economical, and are more or less general.

In so far as the ingots are concerned, side-blow converters cannot compete with the bottom blowing type, but for light-castings foundries the former—notably the Tropenas—has but little competition either from this or other steel-making processes.<sup>17</sup> Latterly, the small basic electric furnace has threatened the deserved popularity of the converter, but there are already indications of a renewed appreciation. Readings over a considerable period have shown the temperature of Tropenas steel to consistently exceed that of electric furnace steel by some 50° C. The greater fluidity, however, appears to be only partly due to this factor of temperature.

### Description of the Tropenas Converter To-day

The converter is of 1½-3½-ton capacity and consists of a sectionally hexagonal steel shell lined with silica bricks and ganister and mounted on two substantial elevated trunnions, one of which is hollow for the passage of cold air to a wind box. The base has a sectional shape of a truncated cone and is detachable. The wind box is mounted around one side of the vessel and consists of a steel case containing a set of silica-tuyere blocks, shaped at the top to the curvature of the converter and perforated lengthwise with holes of 1½ in. to 2 in. for admitting air through to the surface of the molten metal. The tuyeres are set perfectly perpendicular to the axis of the vessel, an error of a degree or so prolonging the blow and leading to cold metal.<sup>18</sup>

The brick lining of the cylinder is about 9 in. thick except at the tuyere side, where it is some 12 in. The bricks are coated with ganister material to a depth of about 1 in. The base and mouth may have a rammed lining of ganister material in place of silica bricks. A conical-shaped internal base gives hotter metal than a square design, which tends to restrict the surface area. An over-large surface area, however, is to be avoided since the oxidation becomes too fierce, leading to excessive fusion losses and poor "life."

Given reasonable control, the acid Tropenas process now readily provides steel of such superior properties and at so rapid a rate as to fully meet rigorous casting shop requirements at competitive cost. These requirements are for molten steel of a high tapping temperature, with good "life" or retentivity, and containing the minimum of oxide, with less than 0·05% of sulphur and of phosphorus, and with carbon and manganese closely within desired limits. The production of such metal demands sound technique and an adequate supply of consistently controlled cupola metal at a temperature exceeding 1,400° C., and it is proposed to consider the underlying factors individually.

*Cupola Furnaces.*—Of the various processes for remelting pig iron, that carried out in the cupola is by far the most common and is particularly suited to providing the comparatively small amount of molten metal required for the Tropenas converter, since a steady supply of an appropriate grade is furnished at low cost.

Since its inception some 150 years ago, the cupola has undergone various constructional modifications, resulting in a more or less standardised design, and in a few special types yielding a higher tapping temperature and requiring rather less fuel. Before passing to recommendations for the normal cupola it may be of interest to summarise these special types.

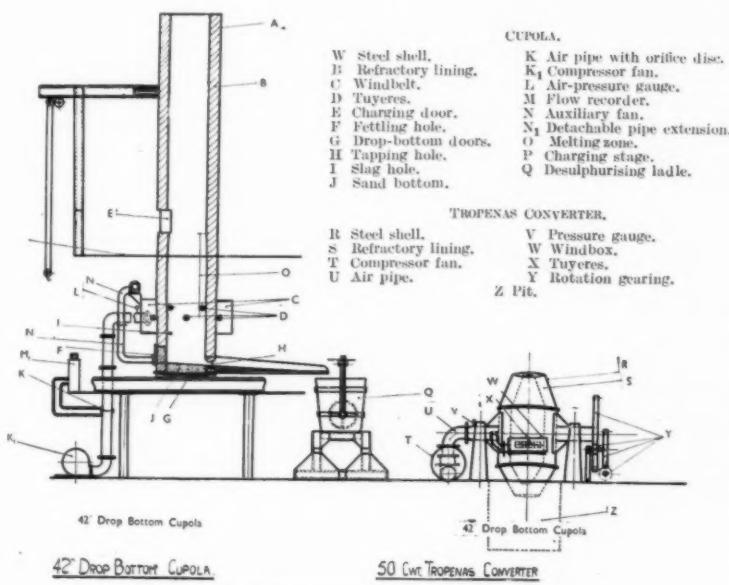
They may be considered in two classes, viz., those supplied with secondary air to minimise the waste of carbon monoxide, and those having a pre-heated blast. Of the former type the balanced blast cupola, introduced by Fletcher and developed by the B.C.I.R.A., has earned rapidly increasing adoption in this country. A very efficient balance of air supply is obtained by means of adjustable tuyeres, of which there are two or three auxiliary rows in addition to the main row. In the continental "Poumay" a spiral of adjustable small tuyeres above two rows in the wind belt serves to pre-heat the charge. Hot-blast cupolas are not favoured in this country. The Griffin type is the American counterpart of the Schurmann cupola used in Germany some

15 *Iron Age*, 79, 1,711; *J.I.S.I.*, 1907, III, 457.  
16 A. Simonson, *Iron and Coal Trades Review*, 1909, **78**, 149; *J.I.S.I.*, 1909, I, 632.

17 M. William and Longmuir, "General Foundry Practice," (Griffin, 1935.)

years ago, heat from the exhaust gases being utilised in preheating the blast to 300°—400° C. The Moore hot-blast cupola, another type in use in the United States, has vertical cast-iron tubes inside the lining above the melting zone which preheat the blast to 150°—180° C. Externally fired stoves are used for heating the blast supplied to other types.

It is necessary to maintain reasonable control of the composition of the cupola iron to be converted. The



A Typical Tropenas Converter Plant

contents of silicon and phosphorus are of greatest consequence, since the oxidation of silicon is one of the main sources of heat in the converter process, whilst phosphorus, which has an embrittling effect, so far from being removed, is actually concentrated by the loss of iron during the melting process. Unless the resultant steel is to be dephosphorised, the average phosphorus contents should not exceed 0·05%. Phosphorus has a hardening and embrittling effect on steel, resulting in poor hot-working qualities. It also causes surface sponginess. Its injurious influence is accentuated by a low-manganese or high-carbon content. Where high ductility is required the steel should contain not more than 0·05% phosphorus, and the further the content is below this limit the better. Its hardening effect may be utilised somewhat in low-carbon, high-strength steels, an increment of 0·01% phosphorus increasing the yield point by a third of a ton per square inch, but resistance to impact falls rapidly when 0·065% is exceeded. The low-phosphorus scrap obtained from basic electric furnaces is ideal for mixing with the pig iron charge.

The average silicon content of the metal charge should be about 2%, but, as the cupola and converter become increasingly hot during the day, the average silicon content of the charge should be reduced to about 1·3%. If the silicon content is too high (over 2·3%) the blow is unduly prolonged. The melting of low-silicon iron lessens the life of the lining. Where the pig

iron is of low-silicon content the requisite amount of ferro-silicon is added. The 45–50% grade has a composition of which the following is typical:—

C	Mn,	S,	P,	Al,	Ti,	Mg,	Ca,
0·03	0·31	0·01	0·019	0·58	0·086	Trace	0·06

Although desirably low in impurities, there is a pronounced melting loss, a disadvantage not attaching to the low-grade alloy containing 12–14% of silicon, but this grade is liable to have a high-phosphorus content. It is better practice to adjust the silicon content of the cupola charge than to make subsequent additions to the converter.

The manganese content is normally less than 0·8%, but a small proportion of manganese steel scrap is sometimes included in the charge in order to provide steel of a higher temperature. Too low a manganese content (< 0·5%) tends to give a thick, viscous slag. If too high (> 0·9%) the converter lining suffers excessive attack. The sulphur content of the metal charged into the converter is of great importance, since the element is not removed; but as it is usually essential to desulphurise the metal obtained from the cupola, the average sulphur content of the original charge is not of much consequence; it should not, however, exceed 0·07%. The main consideration in regard to the carbon content is that a minimum value of 3% is advisable in order to give good fluidity.

Losses during melting are: silicon, 10–15%; manganese, 15–20%. Normally there is an increment in the sulphur and phosphorus contents.

Day-to-day analysis of each heat for carbon, silicon, manganese, sulphur and phosphorus should be carried out. Each spoon sample should be clearly stamped with its progressive heat number as soon as cold enough. A partitioned metal box kept near the cupola helps to prevent mixing of samples. Carbon and sulphur may be accurately determined simultaneously by volumetric combustion, whilst silicon, manganese and phosphorus are rapidly estimated by means of the Spekker photoelectric absorptiometer.

Limestone is used at the rate of 48–60 lb. per ton of metal melted: a deficiency increases the loss of metal and causes serious increments in sulphur content, whilst an excess results in serious attack of the lining. Fluorspar serves primarily as a flux for the slag, thus preventing an abnormal sulphur pick-up. Bettendorf and Wark<sup>19</sup> have shown that whilst the lime content is the main factor in the desulphurisation capacity of slags, its action is greatly increased by solvents such as fluorspar, and Schwerin<sup>20</sup> observed that the consequent increase in basicity and activity favoured desulphurisation.

(To be continued.)

<sup>18</sup> Kain and Sanders. "The Production of Uniform Steel for a Light Castings Foundry." Inst. Brit. Fils., 39th Annual Conference, June, 1942.  
<sup>19</sup> Bettendorf and Wark. *Stahl und Eisen*, June 16, 1932, 577; June 23, 1932, 606.

<sup>20</sup> Schwerin. *Metals and Alloys*, 5 (1934), 61, 83.

# Chromium-Manganese Stainless Irons

*An investigation on the austenitic iron-chromium-manganese alloys is described, and the engineering properties and corrosion resistance of these alloys are considered in relation to their composition, structure and treatment.*

**D**UE to war conditions both nickel and manganese are strategic materials, and their use has to be conserved. The position with regard to nickel is more critical than with regard to manganese. Considerable interest has therefore been shown recently in stainless irons and steels in which part, or all, of the nickel is replaced by manganese. An investigation by J. M. Parks\* on the austenitic iron-chromium-manganese alloys is therefore of practical value in the engineering properties and corrosion resistance of these alloys are dealt with in relation to their composition, structure and treatment.

The alloys tested were made from Armeo iron, electrolytic manganese and low-carbon chromium. The electrolytic manganese was carbon free, and the chromium contained 0.005% carbon. All the alloys were melted in a 5-lb. basic high-frequency furnace, the iron and the chromium being melted first under a glass slag, and then the manganese was added after practically removing the slag. The different alloys were cast into 2,000-grm. ingot moulds, and the ingots were machined to remove surface defects and then forged in the temperature range 980° to 1,095° C. After forging, the alloys were hot-rolled into  $\frac{1}{4}$  in. rod.

Irons containing 12, 20 and 30% of manganese with 12% of chromium and irons containing 12 and 20% of manganese and 5% of chromium were made. In all the irons the carbon content was kept as low as possible. A microscopic examination was made in order to determine the alloy structure so that the structure could be correlated with the physical properties. The hot rolled rod was examined, as well as specimens which had been furnace-cooled and water-quenched after a 2-hour heat-treatment at 980° C. The magnetic properties, hardness, the effect of cold work on the alloys, and the corrosion resistance of the alloys were also determined.

The microstructure of the hot-rolled rods showed a very fine-grained structure, which appeared to account for the varying results obtained from those rods. The water-quenched specimens showed a duplex structure of austenite and rejected ferrite for all of the compositions which were investigated. The rejected Widmonstätten structure was ample evidence of the duplex structure obtained. The rejection of the ferrite in the water-quenched alloys was unusual, in that all similar alloys previously investigated showed no ferrite rejection in the composition range. This effect was probably due to the absence of carbon in the alloys tested, and indicated that important physical property changes might be expected by the presence, or absence, of small percentages of carbon. Comparison of the structures of the various irons showed that in the range 5 to 12% chromium and 12 to 30% manganese increasing chromium content had little influence on the amount of ferrite rejected, while increasing manganese content definitely suppressed the decomposition of the austenite. The furnace-cooled alloys showed the same general

structure as did the water-quenched alloys, although in the 12% chromium, 30% manganese alloy it was doubtful if there was any rejection of ferrite as the structure appeared to be a single phase.

The presence of the ferritic phase was detected by use of a magnet, since the ferritic phase is the only phase which was ferro-magnetic in the system tested. It was found that the magnetic attraction was always less as the manganese content increased, and this verified the microscopic examination which showed that manganese increased the stability of water-quenched austenite. The variation of the magnetic properties with temperature was also investigated, but the apparatus used was not sensitive enough properly to detect the Curie point. From the data obtained, however, it was found that the Curie point for the 12% chromium, 12% manganese steel was near 595° C., a temperature which agreed with the temperature previously determined at which austenite decomposed into ferrite. Cold-work was found to increase the ferromagnetism of the alloys, a phenomenon which indicated that the austenitic phase was not completely stable and decomposed in the same way as that in some of the 18/8 stainless steels.

To determine the difference in cooling rate during heat-treatment, specimens were cut from each hot-rolled rod and given two different heat-treatments. In one case the specimens were heated to 980° C. for 2 hours in a hydrogen atmosphere and then water-quenched, and in the other case the specimens were furnace-cooled in a hydrogen atmosphere after a 2-hours soaking at 980° C. Vickers-hardness determinations were then made on the heat-treated specimens, when it was found that the difference in hardness between water-cooled and furnace-cooled specimens was well within the limits of error, except in one case. The hardness of the alloys was found to decrease as the manganese content increased, and in this respect confirmed the microscopic examination with regard to the rejection of ferrite, since the amount of ferritic phase is small in these steels, and the decomposition of the ferritic phase into the compound Fe-Cr would have little influence on the hardness of the resulting steels.

The influence of cold-work was determined by examining the change in ultimate breaking stress, elongation, electrical resistivity and hardness. The specimens for cold-rolling were prepared from hot-rolled  $\frac{1}{4}$ -in. rod by repeated cold-rolling and annealing at 980° C. Specimens were tested after annealing, and after a 10, 20, 30, 45, 60, 75 and 90% reduction in area. For a given percentage reduction in area the ultimate strength dropped as the manganese content increased, thus indicating that the work-hardening characteristics of the lower manganese alloys was greater. The influence of manganese upon the 5% chromium alloy was to increase the ultimate strength. The percentage elongation values for the annealed alloys showed an increase as the manganese content increased, but were only

slightly influenced by the percentage of chromium. Alloy content also had little if any influence upon the elongation after a reduction in area of over 40%.

On cold-working, the electrical resistivity increased and then approached a constant value as the percentage of reduction in area produced by cold-rolling increased. When the metal was overworked the resistivity increased rapidly, indicating that rolling cracks had been produced. The resistivity also increased as the chromium and manganese contents increased, but the hardness was found to decrease with increasing chromium and manganese, which appeared to indicate that in the alloy ranges investigated the chromium and manganese tend to decrease the amount of rejected ferrite either by increasing the stability of the austenite or by promoting the decomposition of the ferrite. As the cooling rate tests indicated, the decompositiof ferrite had little influence on the hardness of the alloys, it would appear that the primary effect of chromium and manganese must be the stabilisation of the austenite.

The alloys were tested in several corrosive media. A solution consisting of 8% sulphuric acid and 1% copper sulphate was found to dissolve the alloys rapidly at normal temperature. A solution using the same

normality and hydrogen iron-copper ion concentration ratio was made, using in one case a chloride ion as the anion, and in the second case a nitrate ion. The chloride solution corroded the test specimens very rapidly, while the nitrate solution did not appreciably attack the specimens after a 48-hour period. Micro-examination showed no intercrystalline corrosion to occur with any of the alloys. The commercial use of chromium-manganese stainless irons may be of some importance, but in the present stage of development the ultimate strengths of these cold-work irons are not equal to the ultimate strengths of the cold-worked chromium-nickel irons. Additions of molybdenum, titanium and other elements, however, may be found to increase the strength of chromium-manganese irons. Chromium-manganese irons have equal, if not better ultimate strength, in the annealed condition when compared with chromium-nickel irons in the same conditions and this factor may be of importance in the consideration of these irons for welded structures or for casting purposes. Further research on these irons with respect to carbon additions is being carried out, and it is hoped that by proper heat-treatment and cold-work, followed by heat-treatment, an ultimate strength equal to the chromium-nickel steels may be attained.

## Silicon-Bronze Castings

*Problems encountered in working with silicon bronze, which is being increasingly used in the place of tin-bronze, are considered, and attention is directed to the use of high-frequency furnaces for melting this alloy. Some theoretical aspects, connected with the production of serviceable castings, are discussed.*

THE scarcity of tin at the present time, and the necessity of conserving supplies, has resulted in a large replacement of tin bronzes by other alloys. Among these alloys silicon-bronze is perhaps the most important structural bronze available at present. The melting of silicon-bronze, or any other copper alloy, by the high-frequency coreless induction furnace presents problems not found in the standard melting practices, but it has the advantage of speed and easy atmospheric control. A recent description, therefore, by E. Portman\* of the practical problems encountered in working with silicon-bronze, both in the foundry and in the machine-shop, and which describes the use of high-frequency furnaces for melting this alloy is of interest to metallurgists and engineers, particularly as many of the theoretical aspects have been neglected, and the primary task of making serviceable castings in the shortest possible time dealt with.

The melting equipment in the foundry in which the tests were carried out consisted of an Ajax Northrup coreless induction furnace of the lifting coil type. Rapid melting was obtained, in that a 180-lb. charge of silicon-bronze could be brought to the proper temperature in 13 to 14 mins. Green-sand moulds were used for some castings, and skin-dried moulds for larger castings. Chills were liberally applied on heavy sections, and risers were made larger than for gunmetal castings, and were designed so that the metal in the riser was the last to solidify. Large castings were cast between 1,040° and 1,095° C., and smaller castings between 1,120° and

1,175° C. All physical test-pieces were cast in green-sand moulds.

In melting, the charge was made up of copper, silicon-copper hardener, zinc and tin. The copper and hardener were melted first and the tin and zinc last. Satisfactory melts were obtained using a hot crucible fitted with a cover, and by adding about 2 lb. of 15% phosphor-copper per 100 lb. of metal after the charge was removed from the furnace, and prior to pouring, and by omitting charcoal and liquid fluxes, which were used without success in the first melts. Castings of fine uniform grain and free from porosity were obtained having a tensile strength of 21·6 to 23·0 tons per sq. in., a yield point of 7·8 to 8·8 tons per sq. in., an elongation of 23 to 35%, and a Brinell hardness of 74 to 85. The composition of the bronzes cast averaged 91·71% copper, 3·69% silicon, a trace to 1·72% iron, a trace to 0·38% manganese, and 3·54% zinc.

First reports from the machine shops indicated that the silicon-bronze alloy was hard and brittle and dulled the cutting tools excessively. This difficulty was overcome by reducing the residual phosphorus content of the bronze from 0·30 to 0·15%, and thereby lowering the amount of the extremely hard copper-phosphide constituent. As the melting technique was improved through familiarity with the alloy, the phosphor-copper additions were reduced to 1 oz. per 180 lb., melted with the resultant lowering of residual phosphorus to but a trace without adversely affecting the physical properties and sound structure, and at the same time further improving the machinability of the castings.

Experimental melts were cast using a charge consisting of 77 parts of copper, 20 parts of a hardener containing 70% copper, 20% silicon, and 10% iron, and 3 parts of zinc. Varying amounts of scrap from this mixture were added to the charges, and sound castings with good physical properties were obtained from all the melts, including those with 100% scrap. Scrap from defective castings, when remelted under proper conditions, produced sound castings with excellent tensile properties. Using a hardener containing 90% copper, 10% silicon, castings were obtained having a lower tensile strength, yield point and Brinell hardness, but a higher elongation than when using the hardener containing higher silicon and iron. The use of pre-alloyed ingots in preference to a charge consisting of copper, hardener, and zinc showed three advantages. Fewer weighing operations saved time and reduced errors in making up the furnace charge, lowered the melting time for a 180-lb. charge by 2 to 3 mins., and produced less dross during the melting.

In processing silicon-bronze castings special difficulties were found to arise. In soldering silicon-bronze castings to steel shells, the gas flame, by oxidising the silicon at the surface, produced an oxidised area over which the lead-tin solder would not spread, a condition which was overcome by immersing castings in 5% hydrochloric acid at normal temperature for 3 to 5 mins., before the soldering operation. In melting, some difficulty was encountered by the accidental mixing of scrap silicon-bronze with scrap gunmetal, and a special test had to be devised for the identification of the scrap metal. For the test, one drop of a 1 to 1 nitric-acid solution was placed on the cold sand-blasted or machined surface of the metal and the silicon-bronze identified by a dark coloration with blue-black border in distinction to a light-blue coloration obtained with gunmetal. Some trouble was also experienced with castings in which there were abrupt changes in section thickness, and chills and generous fillets had to be provided to obtain a proper temperature gradient during solidification. To provide for the higher shrinkage and greater fluidity of silicon-bronze when compared with gunmetal, and in order to reduce turbulence in casting the metal, special gates and risers had to be used in casting and castings had to be properly fed.

In view of the fact that some silicon-bronze castings were joined to steel and the fabricated parts were immersed in sea-water, a series of corrosion tests were made. The relative susceptibility of steel to corrode with silicon-bronze and gunmetal was determined by measuring the electrolytic potentials in a 3% sodium-chloride solution of two silicon-bronzes and a gunmetal with low-carbon steel and nickel-chromium-molybdenum steel. From the results obtained there was little difference in the corrosion-resisting properties of the three alloys. Silicon-bronze made with the hardener containing silicon and iron appeared to have the best resistance.

In general, the results of the various tests showed that the sound silicon-bronze castings with high-physical properties can be obtained either by the use of hardeners or by re-melting ready-alloyed ingots. High-frequency induction melting offers no serious difficulties once the proper technique has been established, but it is emphasised that for consistently good results it is highly important to melt the metal in a hot crucible fitted with a cover. With good foundry practice production castings

were produced to withstand hydraulic pressure tests up to 300 lb. per sq. in., and air pressure tests up to 95 lb. per sq. in.

### Transformer Welding Equipment

A RECENT publication by General Electric Co. describes a number of single and double operator portable welding sets which are the result of many years of experimental and development work and which incorporate a number of features that have contributed largely to reliable and efficient operation of the sets under severe working conditions. Several types are discussed, and much useful information and data are given. Copies of this booklet may be obtained from the General Electric Co., Ltd., Magnet House, Kingsway, London, W.C. 2.

### Sifbronze Welding

THE Suffolk Iron Foundry (1920), Ltd., Stowmarket, have issued a folder which compares the operations of "Sifbronzing" and brazing. The former is a welding process, although there is a similarity between the two processes in view of the fact that both rely upon the adhesive strength of the jointing alloy to the surface of the parent metal. In neither case is there any fusion of the parent metal.

The contrasting features are that Sifbronze welding requires a definite manipulative technique involving the use of a directly applied highly concentrated heating flame together with a filler rod of closely controlled chemical composition, and any variation in the technique or composition may be detrimental to good workmanship.

The filler rod is a 60/40 copper-zinc alloy with a specified silicon addition, and it is applied for all kinds of joints on metals and alloys with a fusion temperature in excess of 800°C. The process is especially suitable for welding cast iron in which penetration of the parent metal takes place, forming a diffusion zone which increases the strength of the junction formed.

### Inspection Problems

THE detection of cracks, flaws, porosity, etc., in non-ferrous metals presents problems for the inspection staff. The use of fluorescent materials and ultra-violet radiation are being applied to these problems as an aid to visual examination. These methods are applied in an inspection process known as "Hyglo," by which articles to be inspected are dipped into a solution which fills the flaws and cracks with a fluorescent material and then examined under an ultra-violet lamp. Defects that are present are then revealed as vivid green lines or spots against the dark background of the non-fluorescent parts of the article. The solution used is self-regenerating, and never becomes contaminated or saturated, consequently losses and replacements are negligible.

A further development is the production of a fluorescent magnetic material for use instead of the normal black magnetic ink; cracks are readily picked out as a vivid yellow line against a dark background, greatly facilitating detection by increasing the contrast. This material is supplied ready mixed and can be used with any type of magnetiser. These materials have been developed by High Grade Metal Tests, Ltd., 24, Marshalsea Road, London, S.E. 1, from whom further particulars may be obtained.

# Directional Characteristics of Single-Section Structure Copper Strip

By Maurice Cook, D.Sc., Ph.D., and T. Ll. Richards, B.Sc., Ph.D.

*The resolved shear on the slip planes in slip directions has been calculated in terms of the applied stress in various directions for copper strip with the single-texture type of structure, which resembles that of a single crystal. These values have been correlated with tensile strength and elongation values in different directions, and with the earing effects of cups cut from the strip. This report of the investigation is reprinted from the Journal of the Institute of Metals.\**

In a previous investigation into the effect of progressively increasing cold-rolling reductions, and of subsequent annealing on the structure and properties of H.C. copper, the authors have shown that cold-rolling develops a preferred orientation of crystals, which becomes more pronounced with increasing rolling reductions. The crystals take up one or other of two orientations which have a twinned relationship, such as the (110) plane is parallel to the strip surface, and either the [112] axis or the [112] axis is parallel to the rolling direction. The effect of annealing strip cold-rolled with reductions in thickness up to about 50% is to develop a random orientation of crystals, and such strip is substantially free from directional properties. Strip cold-rolled with reductions in excess of about 50% recrystallises on annealing either to form a double-texture type of structure, the orientations of which approximate to those present in the rolled strip prior to annealing, or to form a single texture in which all of the crystals are orientated with a {100} plane parallel to the strip surface and a <100 axis> in the rolling direction. Which type of structure is present in the annealed strip, and in what relative proportions they occur, depends mainly on the grain-size of the strip before rolling, and on the magnitude of the rolling reduction. Small initial grain size and large rolling reductions result in a completely single-texture structure being formed when the material is annealed. Although copper strip having a structure of the double-texture type exhibits some directionality, the most pronounced variation in mechanical properties occurs in single-texture copper strip, and in the present investigation further attention has been given to the directional characteristics of the latter type of material. The single-texture structure resembles that of a single crystal, and the shear stresses which are developed on slip planes during tensile tests on specimens cut in different directions relative to that of rolling can be analysed and correlated with the observed variations in mechanical properties.

## Analysis of the Shear Stress on Slip Planes

In Fig. 1 is shown the projection of the poles of the octahedral or slip planes with respect to the surface of copper strip having a single-texture structure. There are four sets of slip planes, symmetrically situated about the rolling direction OZ, and their poles are numbered 1, 2, 3 and 4 in Fig. 1.

If the normal to the pole figure and the directions in

the strip parallel and transverse to the rolling direction are taken as the axes of co-ordinates, then the direction cosines of the set of slip planes 1 are  $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$ . If a tensile stress  $T$  be applied in a direction OA in the strip surface making an angle  $\alpha$  with the rolling direction, then the angle  $\phi$ , which the stress  $T$  makes with the normal OI to the slip planes 1, is given by the equation :

$$\cos \phi = 1/\sqrt{3} \cdot \sin \alpha + 1/\sqrt{3} \cdot \cos \alpha,$$

and the shear stress on the slip planes

$$= T \sin \phi \cdot \cos \phi$$

$$= \frac{T}{3} (\sin \alpha + \cos \alpha) \sqrt{2 - \sin 2\alpha}.$$

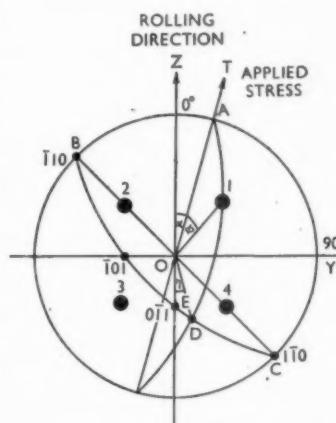


Fig. 1.—Projection of the poles of the octahedral or slip planes with respect to the surface of copper strip having a single-texture structure.

The direction of the shear stress may be found in the following way. If BC be the diameter of the pole figure at right angles to OI, then the great circle through B and C,  $90^\circ$  removed from 1, is the section of the slip plane 1. The direction of the shear stress on this plane, due to the stress  $T$ , will lie in the plane containing the direction OA and the normal OI to the slip plane—that is, in the plane defined by the great circle through

A and 1. The point D, where this great circle meets the great circle representing the slip plane 1, gives the direction OD in which the shear stress is acting. For a face-centred cubic structure there are three slip directions or (110) axes in each slip plane, and the shear stress must be resolved along the nearest slip direction OE. Let the angle DOE be  $\eta$ , then the shear stress on the slip plane resolved in the slip direction OE

$$= \frac{T}{3} (\sin \alpha + \cos \alpha) \sqrt{2 - \sin 2\alpha} \cdot \cos \eta.$$

The value of the angle  $\eta$  for any value of angle  $\alpha$  can easily be determined by means of a stereographic net.

\* M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1940, 66, 1; *ibid*, 1941, 67, 205.

In Table I the values are given of the resolved shear stress on the 1 slip plane in terms of the applied stress  $T$  for values of  $a$  ranging from  $0^\circ$  to  $360^\circ$ . Since the poles 2, 3 and 4 are  $90^\circ$ ,  $180^\circ$  and  $270^\circ$  removed from the pole 1, the resolved shear stresses on the 2, 3 and 4 planes due to tensile stresses in directions making angles ranging from  $0^\circ$  to  $90^\circ$  with the rolling direction will be equal to shear stresses on the 1 slip planes for values of  $a$  ranging from  $90^\circ$  to  $180^\circ$ ,  $180^\circ$  to  $270^\circ$ , and  $270^\circ$  to  $360^\circ$ , respectively. In Fig. 2 are plotted the values of the resolved shear stresses on the four sets of slip planes due to a tensile stress  $T$  applied at angles ranging from  $0^\circ$  to  $90^\circ$  with the rolling direction.

TABLE I.—RESOLVED SHEAR STRESS ON SLIP PLANES DUE TO APPLIED STRESS  $T$  IN VARIOUS DIRECTIONS.

Direction of Applied Stress $T$ .	Shear on Slip Plane $\times T$ .	Direction of Applied Stress $T$ .	Shear on Slip Plane $\times T$ .	Direction of Applied Stress $T$ .	Shear on Slip Plane $\times T$ .	Direction of Applied Stress $T$ .	Shear on Slip Plane $\times T$ .
$0^\circ$	0.408	$90^\circ$	0.408	$180^\circ$	-0.408	$270^\circ$	-0.408
$10^\circ$	0.467	$100^\circ$	0.387	$190^\circ$	-0.467	$280^\circ$	-0.387
$20^\circ$	0.493	$110^\circ$	0.314	$200^\circ$	-0.493	$290^\circ$	-0.314
$30^\circ$	0.481	$120^\circ$	0.205	$210^\circ$	-0.481	$300^\circ$	-0.205
$40^\circ$	0.439	$130^\circ$	-0.0704	$220^\circ$	-0.439	$310^\circ$	-0.0704
$45^\circ$	0.408	$135^\circ$	0	$225^\circ$	-0.408	$315^\circ$	0
$50^\circ$	0.439	$140^\circ$	-0.0704	$230^\circ$	-0.439	$320^\circ$	-0.0704
$60^\circ$	0.481	$150^\circ$	-0.205	$240^\circ$	-0.481	$330^\circ$	-0.205
$70^\circ$	0.493	$160^\circ$	-0.314	$250^\circ$	-0.493	$340^\circ$	-0.314
$80^\circ$	0.467	$170^\circ$	-0.387	$260^\circ$	-0.467	$350^\circ$	-0.387
$90^\circ$	0.408	$180^\circ$	-0.408	$270^\circ$	-0.408	$360^\circ$	-0.408

### Experimental Work

Copper strip with a completely single-texture structure was prepared from an ingot of H.C. copper of the following composition: copper, 99.95%; oxygen, 0.044%; silver, 0.003%; and iron, 0.001%. The ingot, which was  $3\frac{1}{2}$  in. thick, was hot-rolled to 2 in., cold-rolled to 1.5 in., annealed for  $2\frac{1}{2}$  hours at  $530^\circ\text{C}$ , cold-rolled to 0.62 in., and annealed for 2 hours at  $525^\circ\text{C}$ . At this stage the grain-size of the strip was 0.03 mm., and it was cold-rolled to a thickness of 0.031 in. (95% reduction) and annealed for 1 hour at  $550^\circ\text{C}$ . X-ray and microscopic examination of the structure of the finally annealed strip showed that it was entirely of the single-texture type.

TABLE II.—MECHANICAL PROPERTIES OF SINGLE-TEXTURE COPPER STRIP IN VARIOUS DIRECTIONS.

Direction of test-piece relative to rolling direction	$0^\circ$	$11^\circ$	$22^\circ$	$34^\circ$	$45^\circ$	$56^\circ$	$67^\circ$	$79^\circ$	$90^\circ$
Tensile strength, tons/in. <sup>2</sup>	11.05	10.2	10.6	10.6	12.0	10.7	19.05	10.4	11.3
Elongation <sup>a</sup> on 2 in.	22	39	54	60	76	61	53	39	24
Calculated resolved shear tons/in. <sup>2</sup>	4.51	4.81	4.92	4.99	4.90	5.03	4.94	4.90	4.60

Standard tensile test-pieces (B.S.S. No. 485-1934) were cut from the strip at various angles with the rolling direction ranging from  $0^\circ$  to  $90^\circ$ . The mean values of the tensile strength and the elongation obtained from six separate determinations are given in Table II and plotted in Fig. 2.

The tensile properties of copper strip having the single-texture structure differ considerably from the usual values obtained with copper strip having a structure of randomly orientated crystals, and the strip possesses very marked directionality in elongation and appreciable, although less marked, directionality in tensile strength. The low strength of the strip is due to the fact that its structure closely resembles that of a single crystal, the strength of which is well known to be lower than the strength of the corresponding polycrystalline material. The variation in mechanical properties of the copper strip having a single-texture structure is quite symmetrical about the  $45^\circ$  direction,

and certain features of the tensile strength curve and the elongation curve can be correlated with those of the shear-stress curves plotted in Fig. 2.

### Correlation of Results

As will be seen from Fig. 2, variations in the tensile-strength values follow inversely the variations in the resolved shear on the slip planes 1 and 3; that is, the slip planes upon which the resolved shear is greatest for all positions of test-piece from  $0^\circ$  to  $90^\circ$ . The tensile strength value is at a maximum for directions of the applied stress in which the resolved shear on the slip planes 1 and 3 is a minimum, that is, at  $0^\circ$ ,  $45^\circ$  and  $90^\circ$  to the rolling direction, and the tensile strength is a minimum for directions of the applied stress for which

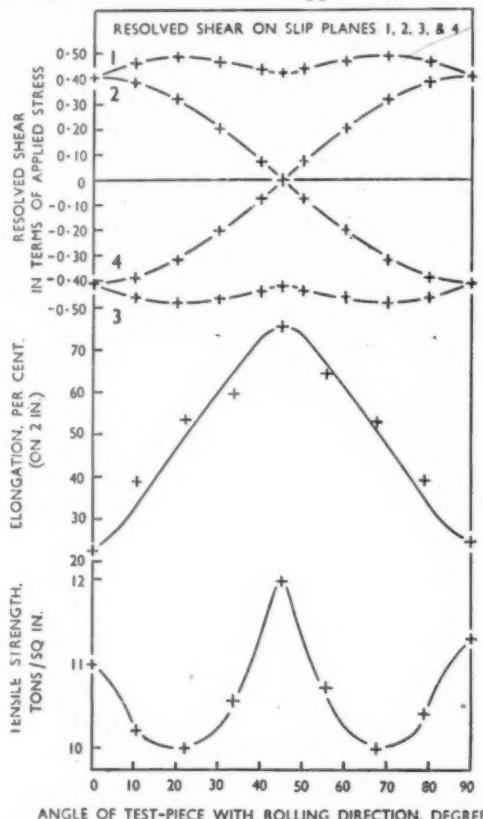


Fig. 2.—Effect of rolling direction on mechanical properties.

the resolved shear is a maximum on the slip planes 1 and 3; that is, at about  $22^\circ$  and  $68^\circ$  to the rolling direction. The connection between the tensile strength of the strip in different directions and the resolved shear stress on the slip planes of maximum resolved shear stress is brought out more clearly if the resolved shear stress for any direction of the applied force is calculated in terms of ultimate breaking stress in those directions. In Table II are given the values of the resolved shear stress, so calculated, and it can be seen that within the limits of experimental error the value of the resolved shear stress on the operating slip planes required to cause fracture is constant for all directions of test-piece, excepting the  $0^\circ$  and  $90^\circ$  directions. For single crystals of various metals it has already been

shown that a constant shear stress is required on the operating slip plane to produce a given extension regardless of the orientation of the crystal.

Comparison of the elongation curve with the resolved shear-stress curves in Fig. 2 shows that the elongation value is a minimum in the  $0^\circ$  and  $90^\circ$  directions, corresponding to the directions of the applied stress for which the resolved shear stress on each of the four slip planes

values upon the slip planes are required in the  $0^\circ$  and  $90^\circ$  directions. In a cupping operation, where the metal of a circular blank is constrained to flow in radial directions, the metal will deform most readily in the directions parallel to the strip surface in which it requires the minimum resolved shear for deformation, and with cups cut from single-texture copper strip this results in earing in the  $0^\circ$  and  $90^\circ$  directions.

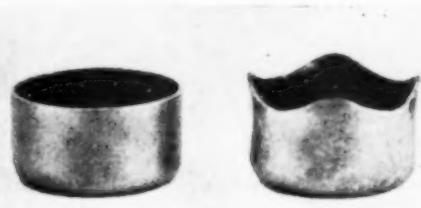


Fig. 3.—Flat-topped and eared cups.

is high and equal in value, whilst the elongation is a maximum at  $45^\circ$  to the rolling direction, the direction of the applied stress for which the resolved shear is zero on two of the slip planes. The ductility of the strip is least in the directions where the applied stress causes all four sets of slip planes to operate simultaneously and greatest in the directions where the applied stress results in slip occurring on only two sets of planes.

When cups are cut from annealed copper strip composed of randomly orientated crystals they have flat tops, but single-texture copper strip yields cups with pronounced waviness or earing at  $0^\circ$  and  $90^\circ$  to the rolling direction. In Fig. 3 are illustrated flat-topped and eared cups, both of which were produced from these two different types of copper strip rolled from one ingot, the single-texture strip being that used for tensile tests, the results of which are given in Table II. The positions of the ears correspond with the positions of minimum elongation in the strip and also with the  $0^\circ$  and  $90^\circ$  maxima of the tensile strength. The calculated values of the resolved shear stress, on the planes upon which slip occurs, in terms of the ultimate breaking stress detailed in Table II indicates that, for deformation parallel to the strip surface, the smallest resolved shear

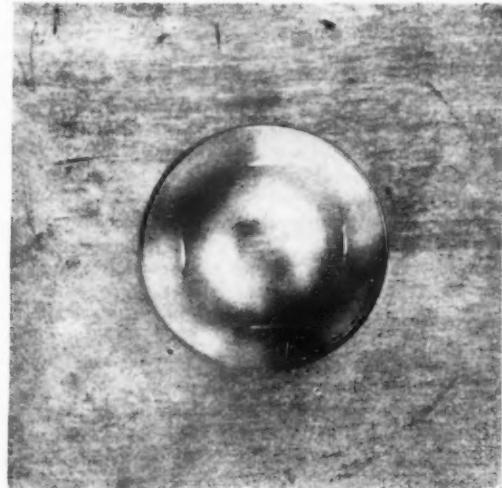


Fig. 4.—Fractures produced in positions corresponding to the directions of minimum elongation.

The weakness of the single-texture-structure strip in the  $0^\circ$  and  $90^\circ$  directions may also be demonstrated very strikingly by the Erichsen test, in which a spherical steel dome is pressed into the strip, the depth of the impression required to cause the first signs of fracture providing an indication of the ductility and drawing quality of the material. If, with copper strip having a structure of the single-texture type, the dome is impressed a little deeper than is necessary to cause the first sign of failure, four fractures, as shown in Fig. 4, appear in the  $0^\circ$  and  $90^\circ$  positions corresponding to the directions of minimum elongation and to the positions of ears on cups cut from the strip.

### The Institute of British Foundrymen

The annual general meeting of the above Institute will be held on June 26, 1943, at the Waldorf Hotel, London, W.C. 2. Council and committee meetings will be held on the afternoon and evening of June 25. Following the council meeting, Mr. J. W. Gardom will show a film illustrating the mass production of a manganese steel casting.

The annual general meeting will commence at 9.30 a.m., and following the normal business the Edward Williams' Lecture will be delivered by Dr. S. F. Dorey on "The Contribution of the Steel Founder to Marine Engineering." The afternoon will be devoted to the presentation and discussion of papers, and three sessions have been formed to proceed simultaneously, thus :—

*Session A.*—"The Effect of Casting Conditions on the Properties of a Magnesium Die-Casting Alloy," by Professor W. R. D. Jones, D.Sc.; "Report on a Copper-Antimony-Nickel Gear Alloy," by the Non-Ferrous Sub-

Committee of the Technical Committee; "A Method of Correlating Foundry Production and Quality of Light Alloy Castings," by H. G. Warrington.

*Session B.*—"Some Aspects of the Production of Malleable Iron Castings," by J. Roxburgh; "The Spectrographic Analysis of Cast Iron," by F. B. Ling, J. McPheat, and J. Arnott, F.I.C.; "Meeting the Raw Materials Supply Position," by the Cast Iron Sub-Committee of the Technical Committee; "Industry and Education," by G. L. Harbach and R. Horton.

*Session C (Joint Meeting with the Iron and Steel Institute).*—"Hot Tears in Steel Castings," by C. W. Briggs (American Foundrymen's Association Exchange Paper, to be presented on behalf of the author by P. C. Fassotte); "The Continuous Production of Manganese Steel Castings from the Tropenas Converter," by L. W. Bolton and J. Hill; "A War-time Steel Foundry," by E. Derek Wells and A. Johnson.

# Machining Magnesium Alloys

*An Antiseptic Coolant which Improves Finish and Reduces Fire Risk*

**A**LTHOUGH many erroneous views are held regarding the fire risk and inflammability of magnesium and its alloys, it is generally recognised that a fire risk does exist when small particles, such as are produced in many machining operations, are heated in the course of these operations. When the temperature is high enough the swarf will ignite spontaneously, or as a result of sparking of the tool. Swarf fires caused in this way are not only dangerous, but they are a nuisance and will put a machine tool out of action for a time, depending upon the extent of the fire and the means employed to subdue it.

The usual practice is to machine magnesium and its alloys dry—that is, without a coolant. This is doubtless due to the fact that the material offers very low resistance to the cutting tool, and, since it has a high thermal conductivity, heat generated when cutting is rapidly dissipated. But the tool must be sharp and the cutting speed high to obtain the best results. With the increased use of the range of magnesium alloys and the greatly increased rate of production of machined parts tools may be used in a blunt condition, in which condition it is generally assumed that the fire risk is greater.

The use of a water-base coolant, commonly used when machining other materials, is not satisfactory, since not only would it increase the violence of a fire, should one start, but it would contaminate the swarf by precipitating the oxide and make the recovery of the metal, from the scrap, very difficult. Considerable attention, however, has been given to this question of a suitable coolant for machining magnesium, and after long research and experimental work there seems every likelihood that a satisfactory coolant for this special purpose will soon be available. Tests have been carried out at the works of the Lockheed Hydraulic Brake Co., Ltd., with the helpful co-operation of responsible authorities at these works.

The machine test was made on a cylindrical piece of magnesium alloy (D.T.D. specification containing 86·5% magnesium), about  $\frac{1}{2}$  in. diameter. The first cutting test was made dry using a sharp tool. The cutting speed was 260 ft. per min., depth of cut 0·25 in., and feed 0·003 in. The second test was carried out under exactly similar conditions, but using the coolant. As will be noted in the accompanying illustration, taken from an untouched photograph of the test-piece, a smoother finish is obtained with the aid of the coolant.

In order to test the fire-resisting properties of this coolant, further cuts were made in an effort to cause a fire. A blunt tool was used at the same cutting speed, depth and feed as with the previous tests, using the coolant, but, although every endeavour was made to cause the swarf to fire, neither sparks nor flames were seen. The illustrations show the amount of scoring resulting from this test.

Since the above tests were carried out further machining tests have been made elsewhere, as a result of which it is authoritatively claimed that the finish obtainable on magnesium alloys, when using this coolant, is greatly



Result of machining tests on a magnesium alloy, containing 86.5% magnesium, carried out at the works of the Lockheed Hydraulic Brake Co., Ltd., with and without a fire-preventive antiseptic cooling fluid.

superior to that obtainable when machining the same alloy dry. It was also found that, contrary to the more generally accepted theory that blunt tools cause the swarf to fire, moderately sharp tools have a greater tendency to cause fire. In fact, we understand that machining conditions were determined under which a fire can be caused at will in this manner.

This coolant, which will be marketed under the name "Maxium," has been developed by Edwin Taylor (Chemicals), Ltd., Boardman Chemical Works, London Road, Manchester, 1, and an application has been made for patent rights. In addition to its property of improving the quality of the finish and of preventing fire when machining magnesium alloys, we understand this coolant is also an antiseptic. This is a very important quality, and one which will have a distinct bearing on its successful application. Another important factor is that the use of this coolant is not detrimental to the process of alloy recovery from the swarf, although, as in the case of swarf machined from many other metals and alloys, the use of a centrifuge is advantageous.

# Desirability of Removing Sulphur from Gaseous Fuels for Heating Ferrous Metal\*

By A. Preece, M.Sc.

*The results obtained in a general study of the high-temperature oxidation of steels are considered with special reference to the harmful effects of the sulphur content of the furnace atmosphere. The advantages which result from partial removal of sulphur from the fuel, and the working conditions necessary for the full realisation of these advantages, are indicated.*

WATER-GAS plants and small producers are being installed for use in steelworks where the town's gas supply is inadequate to meet the increased demand for war production. The auxiliary equipment for the removal of sulphur from the gas produced in these units represents a high proportion of the total cost of the plant, and this report was prepared in answer to an inquiry as to how far sulphur removal from gaseous fuel, to be used for heating steels, was advisable or necessary. The information presented has been obtained in a general study of high-temperature oxidation of plain carbon and alloy steels carried out at Leeds University.

## General Considerations

The following conditions apply only in furnaces where the products of combustion of the fuel constitute the furnace atmosphere and are in contact with the heated metal.

(1) It has been found that the addition of sulphur dioxide to typical furnace atmospheres has a profound influence on the scaling characteristics of heated steels. There is usually an important increase in the rate of oxidation with the formation of iron sulphide in the oxide scale.

(2) At tempering and hardening temperatures, i.e., 650° C. to slightly below 900° C., there is no formation of the oxide-sulphide complex: the iron sulphide is distributed as separate particles throughout the scale layer, and there is little or no tendency for sulphide penetration along the crystal boundaries.

(3) At temperatures above 900° C. the sulphide forms a molten oxide-sulphide complex at the scale-metal interface, which penetrates into the metal along the grain boundaries. There is also a change in both the scale produced and its adherence to the metal surface, which may affect the ease of scale removal. It will be appreciated, therefore, that the effect of the sulphur dioxide will vary according to whether the furnace temperature is above or below approximately 900° C.

(4) The presence of free oxygen in the furnace atmosphere is important, in that it minimises the evil effects of sulphur dioxide by preventing the formation of iron sulphide in the scale. It should be stressed, however, that oxygen itself accelerates scale formation in all but high-sulphur-containing atmospheres—hence the presence of oxygen is permissible only if the furnace atmosphere already contains appreciable quantities of sulphur dioxide.

(5) Without a knowledge of the design of the particular furnace in which the steel is to be heated, it is wrong

to assume that if excess air is used in the combustion of the fuel, the furnace atmosphere in contact with all the steel will contain free oxygen. In furnaces of the semi-muffle type and those in which gas and air premixers are used this assumption is undoubtedly true, but if the gas and air enter the furnace chamber through separate flues there may be regions in the vicinity of the gas ports where combustion is incomplete, and steel in these regions would be sealed under conditions where the sulphur would exert its maximum influence.

(6) The rate of oxidation of steel increases exponentially with temperature; hence, temperature control is important, particularly where the furnace temperature approaches the melting point of the oxide scale. When this temperature is reached there is a sudden increase in the rate of scale formation owing to the removal of the partially protective layer of scale as it melts and flows away from the surface of the metal. Indeed, in this region temperature control is perhaps the most important factor governing oxidation, and much of the advantage resulting from sulphur cleaning, atmosphere control, etc., would be lost if at the same time adequate attention was not given to temperature control.

(7) The compositions of the furnace atmospheres obtained by the complete combustion of typical gaseous fuels are shown in Table I.

TABLE I.—FURNACE ATMOSPHERES PRODUCED BY COMPLETE COMBUSTION OF TYPICAL GASEOUS FUELS.

	Products of Complete Combustion.			
	CO <sub>2</sub> , %	H <sub>2</sub> O, %	N <sub>2</sub> , %	SO <sub>2</sub> , %
Crude coke-oven gas, 6.0 grains of sulphur per 100 cub. ft.	10	20	70	0.20
Town's gas, 20 grains of sulphur per 100 cub. ft.	10	20	70	0.007
Producer gas from coal containing 2% of sulphur	17	10	71	0.13
Water gas from coke containing 1% of sulphur	16	20	61	0.05

## Main Factors Influencing the Oxidation of Steel

A general idea of the relative importance of each constituent of a typical furnace atmosphere may be obtained from the following results obtained by heating steel specimens for 1½ hours at 1,150° C. Taking a furnace atmosphere consisting of 10% of CO<sub>2</sub>, 10% of H<sub>2</sub>O and 80% of nitrogen as a basis, then :

Increasing the CO<sub>2</sub> to 20% decreased the oxidation by 25%. Increasing the H<sub>2</sub>O to 20% increased the oxidation by 15%. Adding 0.2% of SO<sub>2</sub> to the above atmosphere increased the oxidation rate 3 times. Adding 4% of oxygen or more to the above atmosphere increased the oxidation rate 2½ times.

It will be realised, therefore, that the important factors governing the oxidation of steel are : (a) Temperature, and (b) composition of the furnace atmosphere,

\* Paper No. 10 1943 of the Alloy Steels Research Committee, published by the Iron and Steel Institute. (Advance copy.)

particularly with regard to the sulphur-dioxide and oxygen contents; and to these must be added (c) the presence of certain alloying elements in the steel.

### The Heating of Steels in Furnace Atmospheres

It will be convenient to consider two temperature ranges, i.e., above and below 900° C. Above this temperature the oxide-sulphide complex which forms in the scale causes intense intercrystalline penetration, which is not so marked at lower temperatures.

(a) *Furnace Temperatures below 900° C.*—In this lower temperature range the presence of sulphur dioxide causes an important increase in the rate of scale formation in atmospheres free from oxygen.

In Table II the increased scaling losses to be expected in changing over from purified to a crude gaseous fuel are shown. Actual scaling losses are given in the second column.

The figures given in Table II refer only to oxygen-free atmospheres. This is stressed, because oxygen itself causes a rapid increase in scale formation and at the same time renders the sulphur dioxide ineffective as a scaling agent. Oxygen also prevents the formation of iron sulphide in the scale.

TABLE II.—INCREASED SCALING LOSSES ON CHANGING FROM PURIFIED TO CRUDE GASEOUS FUEL, TEMPERATURE BELOW 900° C.  
Information contained in this Table has been taken from a thesis presented by Dr. E. Simister to Leeds University for the Ph.D. Degree.

	Steel exposed 1½ hrs. at 850° C.	Metal lost by oxidation in Oxygen-free Furnace Atmospheres (10% CO <sub>2</sub> , 1% H <sub>2</sub> O, 80% N <sub>2</sub> ) containing 0.015% of SO <sub>2</sub> , Oz. per sq. ft.			Increase in Scaling Losses on Changing from Purified to Crude Gas giving High Concentration of Sulphur Dioxide, SO <sub>2</sub> . Increased by factor of -
		0.05%	0.10%	0.20%	
Plain carbon steel	0.57	2½	4	5½	
1.5% Mn steel	0.56	2	3	4	
5% Ni steel	0.33	3	3½	10	
3.5% Ni, 0.75% Cr steel	0.50	2½	3	5	
1% Si steel	0.44	2	2	2	
12% Cr steel	Scale irregular,	2	2	2	
	approx.	approx.	approx.	approx.	

It will be clear, therefore, that sulphur removal will result in minimum scaling only in oxygen-free furnace atmospheres. This may be further illustrated by consideration of the following example. It was found that with a plain carbon steel at 850° C. the addition of 0.10% of SO<sub>2</sub> to an oxygen-free furnace atmosphere caused the same increase in the rate of scale formation as the addition of 2.0% of oxygen; thus, if the working conditions were such that the furnace atmosphere would contain 0.10% of SO<sub>2</sub>, it would be advisable to burn the fuel so as to have 2.0% of oxygen present, because the scaling losses would be the same, there would be little or no sulphide formed in the scale and, further, the scale would be less adherent. If the sulphur-dioxide content of the furnace atmosphere were greater than 0.1%, then the presence of the oxygen would maintain a lower rate of scale formation than would otherwise occur.

In this low-temperature range there is a formation of sulphide particles in the scale, but with the plain carbon and 1.5% manganese steel there was no evidence of intercrystalline penetration of scale or sulphide into the metal, even in atmospheres containing as much as 0.2% of SO<sub>2</sub>.

With the 5% nickel steel, however, when the concentration of the sulphur dioxide approached 0.05% a slight degree of sulphide penetration occurred, which

became more pronounced as the sulphur-dioxide concentration was further increased; in a high-sulphur atmosphere (80% N<sub>2</sub>, 10% CO<sub>2</sub>, 10% H<sub>2</sub>O plus 0.2% SO<sub>2</sub>), after 8 hours heating at 850° C., this intercrystalline penetration extended 0.002 in. into the metal, but when 3% of oxygen was also present there was no penetration of scale. With nickel steels, therefore, the presence of free oxygen is essential if the furnace atmosphere contains sulphur.

The 3.5% nickel, 0.75% chromium steel and the 12% chromium steel also showed slight evidence of intercrystalline penetration when the sulphur dioxide content of the atmosphere reached 0.05%. When oxygen was added to the furnace atmosphere sulphide penetration was prevented, but with the nickel-chromium steel an equally deep intercrystalline penetration of oxide occurred, which might be as troublesome as the sulphide penetration as far as scale removal is concerned.

The high resistance of the 4% silicon steel to oxidation was destroyed by sulphur dioxide, and although the increased scaling was not accompanied by intercrystalline penetration of scale into the metal a subscale formation occurred at the scale-metal interface which would be difficult to remove by the normal descaling processes, and would undoubtedly result in a poor surface finish.

TABLE III.—INCREASED SCALING LOSSES ON CHANGING FROM PURIFIED TO CRUDE GASEOUS FUEL, TEMPERATURE ABOVE 900° C.  
Information contained in this Table has been taken from a thesis presented by Dr. R. V. Riley to Leeds University for the Ph.D. Degree.

	Steel exposed 1½ hrs. at 1,150° C.	Metal lost by Oxidation in Oxygen-free Furnace Atmosphere (10% CO <sub>2</sub> , 10% H <sub>2</sub> O, 80% N <sub>2</sub> ) containing 0.015% of SO <sub>2</sub> , Oz. per sq. ft.			Increase in Scaling Losses in Changing from Purified to Crude Gas giving Higher Concentration of SO <sub>2</sub> in Furnace Atmosphere obtained by Complete Combustion of Gas, SO <sub>2</sub> . Increased by Factor of -
		0.05%	0.10%	0.20%	
Plain carbon steel	5.5	1½	2	3	
5% Ni steel	3.2	1½	2	4	
3.5% Ni, 0.75% Cr steel	3.3	1½	2	3	
1% Si steel	1.7	1½	3	3½	
2% Si, 9% Cr steel	6.6	1½	2	2½	
13% Mn steel	3.1	2	3	4½	
12% Cr steel	6	1½	2	2½	
18% Cr, 2.5% Ni steel	1	1½	2½	3	
18% C, 8% Ni steel	approx. 2	1½	1½	4	
25% Cr, 17% Ni steel	approx.	approx.	approx.	approx.	A protective oxide skin formed which prevented further oxidation even when 0.2% of SO <sub>2</sub> was present.
30% Cr, 7% Ni, 4% W steel					An alumina-rich film which formed in sulphur-free atmospheres was destroyed by SO <sub>2</sub> and rapid scaling occurred.
25% Cr, 7% Ni, 4% W steel					
8% Al steel					

The more highly alloyed steels, such as the 18% chromium, 2½% nickel steel, higher-chromium steels, and an 8% aluminium steel, showed very slight attack when exposed to furnace atmospheres containing as much as 0.2% of SO<sub>2</sub>. A thin skin of protective oxide formed on the surface, which prevented further oxidation.

(b) *Furnace Atmospheres above 900° C.*—The effectiveness of sulphur dioxide in increasing the rate of scale formation becomes greater as the furnace temperature is raised, and at forging temperatures the loss of metal due to oxidation represents an appreciable tonnage of steel. In addition, at temperatures above 900° C. this increased scaling in sulphur-containing atmospheres is accompanied in certain circumstances by deep intercrystalline penetration into the steel of the iron-sulphide/iron-oxide complex which is formed at the scale-metal interface.

Table III has been drawn up in a manner similar to Table II, and shows the increase in scaling losses to be

expected on changing over from a purified to a crude gaseous fuel when burnt to give no free oxygen in the products of combustion. It will be noted that the scaling losses are high even when using a purified gas, and that they are further increased when sulphur is present.

In considering the behaviour of the four resistant steels in Table III, where continued oxidation had been prevented by the formation of an extremely thin chromium-rich oxide skin, the conditions of test should be emphasised, i.e., 1½ hours at a constant temperature of 1,150° C., since it is not known to what extent this high degree of resistance would be retained over long periods of exposure or with fluctuating temperatures. Experiments along these lines are in progress by the author at the present time.

The increased scaling due to sulphur dioxide in oxygen-free furnace atmospheres was accompanied in this higher-temperature range by intense intercrystalline penetration of the oxide-sulphide complex, with the plain carbon, the 13% manganese, the 3·5% nickel 0·75% chromium, and the 5% nickel steel. Penetration was most severe with the 5% nickel steel, in which it had extended to a depth of 0·02 in. after 1½ hours heating at 1,150° C. in a high-sulphur atmosphere containing 0·2% of SO<sub>2</sub>. This degree of penetration would undoubtedly give trouble in forging operations.

No evidence of intercrystalline penetration was found in the 4% silicon, the 3% silicon, 9% chromium, and the 12% and higher chromium steels; sulphide particles were found in the inner layers of the scale, but their only effect seemed to be to produce a more even scale-metal interface.

No oxide-sulphide complex could be found in the scale formed at 1,000° or 1,150° C. in furnace atmospheres containing less than 0·03% of SO<sub>2</sub>; hence there would appear to be little advantage in taking sulphur removal beyond the stage which would give less than 0·03% of SO<sub>2</sub> in the furnace atmosphere, particularly as the cost of sulphur removed increases rapidly as the sulphur content of the fuel becomes less.

Having established a permissible sulphur content in the furnace atmosphere, it is possible to calculate the corresponding sulphur value of the gaseous fuel and so determine the amount of sulphur to be removed from the latter. This has been done for each of the three gaseous fuels, and the results are given in Table IV.

One interesting feature of Table IV is the comparatively small amount of sulphur to be removed from producer and water gas, and, while iron-oxide cleaning plants can be designed for this purpose, a cheaper

TABLE IV.—SULPHUR TO BE REMOVED FROM GASEOUS FUELS.

Fuel.	Ratio of Gas to Air for Complete Combustion.	Critical Sulphur Content of Fuel to give 0·03% of SO <sub>2</sub> in Products of Complete Combustion.	Sulphur to be Removed.
Crude town gas, 600 grains of sulphur per 100 cub. ft. ....	1 : 4	Grains per 100 cub. ft. 90	510
Water gas from coke containing 1% of sulphur (= 108 grains per 100 cub. ft.) .....	1 : 1·75	50	58
Water gas from coke containing 2% of sulphur (= 254 grains per 100 cub. ft.) .....	1 : 1·75	50	204
Producer gas from coal containing 2% of sulphur (= 230 grains per 100 cub. ft.) .....	1 : 1	39	160
Producer gas from coke containing 1% of sulphur (= 100 grains per 100 cub. ft.) .....	1 : 0·8	32	68

method may be found by using ammonia washing towers.

The statement that oxygen added to furnace atmospheres imposes its own influence on the rate of scale formation and renders the sulphur dioxide ineffective is true at forging temperatures, but needs some qualification in the case of a few steels, e.g., with the plain carbon, 13% manganese and 4% silicon steels, the addition of 1–2% of oxygen to the furnace atmosphere containing sulphur dioxide accentuated the accelerating influence of the sulphur dioxide, and it was only with higher oxygen additions that the sulphur dioxide became ineffective. The silico-chromium steel is also an exception, in that the influence of sulphur dioxide and oxygen when present together is roughly the sum of their separate effects.

Experiments have shown that sulphur dioxide maintains its accelerating influence on scale formation up to 1,330° C., and, with steels containing silicon, as this temperature is approached the effect of any oxygen which may be present, instead of replacing the effect of the sulphur dioxide, tends to augment it. No precise information is available for temperatures above 1,330° C.

Apart from its effect on the scaling losses, the presence of oxygen in furnace atmospheres containing sulphur dioxide suppresses the formation of the oxide-sulphide complex in the scale and prevent intercrystalline penetration of the latter into the steel.

### Conclusions

(1) The effect of sulphur-bearing gases in furnace atmospheres is twofold (i) an increase in metal loss due to scaling, and (ii) intergranular penetration of scale.

(2) Both effects are pronounced at temperatures above 900° C., the first being important economically, and the second inimical to good forging properties.

(3) For temperatures above 900° C., sulphur removal is considered essential, but its value is not fully realised unless combustion is so controlled as to avoid the presence of free oxygen in the furnace atmosphere.

(4) For temperatures below 900° C., the loss of metal due to scale formation is not excessive, even with unpurified gas; hence, sulphur removal is not considered essential in this temperature range, except for certain nickel-bearing steels in which intergranular penetration of the oxide may be caused by the presence of sulphur.

(5) Intergranular penetration of oxide-sulphide scale has not been found when the concentration of sulphur dioxide in the furnace atmosphere is reduced to 0·03%; thus, only partial sulphur removal is then called for.

(6) The presence of free oxygen in the furnace atmosphere, although it gives a high rate of scale formation, counteracts the effects of sulphur dioxide and produces a non-adherent type of scale.

The author expresses his thanks to members of the Alloy Steels Research Committee for their helpful discussions, and to Mr. A. Hartley, of Leeds University, and Mr. N. Williams, of Messrs. Humphrey and Glasgow, Ltd., for their assistance.

Mr. Lawrence Levy, who has been chairman of the Board of Directors of George Cohen, Sons and Co., Ltd., since 1928, recently celebrated the fiftieth anniversary of his joining the firm.

# Thickness Testing of Electrodeposits

*Various methods for testing the thickness of electrodeposits are briefly described, but it is emphasised that no thickness test, however accurate, is of any value unless it is fairly and intelligently applied, and the plater must honestly interpret the specifications.*

**I**N general, it is recognised that the protective value of a deposit on a base metal is primarily a function of its thickness. Thus, the best way of specifying the particular degree of protection required from a plated coating is to specify the minimum thickness of deposit which will be acceptable. Gradual appreciation of this fact throughout the electroplating industry has caused plating to thickness specification to become more and more common. Indeed it is now rare to receive a plating order which does not mention the thickness required. Obviously, therefore, thickness testing has become very important, and many methods of determination which have been developed are discussed by Mr. A. W. Wallbank,\* from which is made a selection of the available methods. In many cases, however, not only is the thickness of deposit specified, but the method by which that deposit shall be measured.

## Methods of Thickness Testing

The various methods of thickness testing can usefully be classified according to the units in which the determination is actually made, e.g., whether the method fundamentally involves a direct measurement, a weighing operation, a timing process, or an estimate of magnetic properties.

### Direct Measurement

**Micrometer.**—The simplest method is to use a micrometer. This method is admittedly crude for deposits less than one-thousandth of an inch, but a good vernier micrometer with ratchet stop is a useful tool for quick measurement of quite thin deposits. It is, of course, essential that the same spot of the same article is measured with and without deposit.

**Microscope.**—This method requires elaborate equipment and a skilled operator, but it is of general application. A cross section of the plated article is polished, etched if necessary, and the edge of the exposed deposit measured by microscope.

**Chord.**—This method, which originated in America, is a simple means of increasing the dimension to be measured to a more convenient size. Coatings on flat surfaces are just cut through by a circular grinding wheel of known radius ( $R$ ) by means of a precision grinder. The width of the cut (the chord) ( $C$ ) is accurately measured and the thickness ( $T$ ) computed from the formula

$$T = \frac{C^2}{8R}$$

Curved surfaces of known radius can also be measured by this method. A flat grinding surface is applied to the curved article until the deposit is just cut through. The

same formula as above applies, though in this case  $R$  is the radius of the article.

### Time Methods

**Immersion.**—The simplest form of time method is to immerse the specimen in the reagent and time the period required for penetration. The reagent is standardised against deposits of known thickness, and the rate of penetration at a range of temperatures plotted on a chart. It is then a simple matter to read from the chart the thickness of an unknown deposit at the temperature of the test.

Examples of this method include:—

- (a) B.N.F. test for chromium-plating thickness.
- (b) Olsen and Blum spot test for chromium-plating.
- (c) Preece test for zinc-plating.
- (d) Various shop methods for zinc and cadmium-plating.

**Jet Test.**—This test, which has been developed and standardised by the British Non-Ferrous Metals Research Association, has become very popular in this country. A fine continuous stream of the specific reagent is allowed to impinge on the plated surface until the deposit is penetrated. The time necessary is measured by stop-clock. In order to facilitate observation of the end point the jet can be stopped and restarted from time to time, the clock being stopped and restarted simultaneously. The apparatus has been carefully designed and standardised. The reagent solution is contained in a top funnel carrying a device which maintains a head of 10 in. in order to ensure that the solution is delivered under constant pressure. The jet tube is of standard dimensions and is protected by a guard-tube. The whole apparatus is held on a stand which also carries a clamp for holding the article under test rigidly at the correct angle and distance from the free end of the jet.

**Dropping Tests.**—This method is the American counterpart of the B.N.F. jet test. The only difference is that instead of a continuous stream of reagent impinging on the plated surface, the penetrating solution is delivered from a capillary tube in a series of drops. The apparatus is designed to deliver solution at the rate of 100 drops per minute.

### Magnetic Methods

These methods are more recent and may prove the most valuable of all. They are very rapid and quite non-destructive. They rely on measuring the difference in magnetic properties of the deposit compared with the basis metal.

**Permanent Magnet.**—The attractive force of a permanent magnet is measured by a steel spring and recorded on a dial.

**Electro-magnet Type.**—This type measures the variation in the flux of a magnetic circuit created by the electro-deposited coating.

(Continued on page 98)

# The Conservation in Nickel in Electric-Resistance Alloys

*Attention has been drawn to the necessity for conserving nickel supplies and to restrictions that are being placed on the release of raw materials for the manufacture of high-nickel alloys, particularly the 55-45 copper-nickel type for control resistances, and this article from Monel Notes 27\* describes alternative materials for these applications.*

In view of the urgent need for conserving nickel during the period of the war, we have given a great deal of thought to the possibility of providing alternative materials to the high nickel-containing alloys at present used for control resistances. Unfortunately, the use of these alloys is based on electrical and mechanical characteristics which cannot be wholly repeated with alternative materials and changes made by users will almost inevitably necessitate some compromise in design and performance.

At the moment particular attention is being directed towards saving the nickel used in the production of the nickel-copper alloy Ferry,† the composition of which is given in Table I. The amount involved is substantial for this alloy is widely used for control resistances of all kinds. This use of Ferry is based on the following desirable characteristics :—

Its specific electrical resistance can be maintained within close limits and is of a convenient magnitude, namely, 49 microhms/cm.<sup>3</sup>.

It has a temperature coefficient of resistance which, for all practicable purposes, is negligible.

It has good ductility, which is of considerable value in the drawing of wire to close limits on diameter and in the fabrication of spirals and other forms required by the rheostat manufacturer.

It has reasonably good resistance to corrosion by most of the commonly met corrosive agents, and possesses good resistance to oxidation at temperatures up to 400° C.

It is possible to produce on the wire a closely adhering oxide coating having sufficiently good insulating properties for close-wound resistances of many types.

Of all these characteristics, the one most difficult to reproduce in an alternative material to Ferry is the very low temperature coefficient of electrical resistance. All iron-base alloys have high-temperature coefficients, and most non-ferrous alloys also have temperature coefficients far in excess of that of Ferry. An exception is the nickel-copper-manganese alloy known as "Tarnac," or "Manganin," which has a very low-temperature coefficient and, since it contains only about 4% nickel, would seem an obvious alternative to Ferry. Unfortunately, the supply position of the pure manganese which is required in the production of Tarnac is such that the replacement of Ferry with Tarnac cannot at present be favourably regarded by the Ministry of Supply. Technical difficulties also exist. Tarnac is difficult to manufacture. It is not as stable as Ferry in its resistance properties at temperatures above 250° C. Its corrosion resistance is inferior to that of Ferry. The use of Tarnac is therefore being confined to certain

TABLE I.

Nominal Composition.	Ferry.	80/20 Cupro-Nickel.	Stainless Iron.
	Nickel, 44-45% Copper Balance.	Nickel, 20% Copper, 80% Balance.	Chromium, 12-14% Iron Balance.
Specific electrical resistance— Microhms/cm. <sup>3</sup> at 15° C.	49	27	56 <sup>a</sup>
Temperature coefficient electrical resistance.	Negligible.	0.0002-3 per °C. from 15°C. to 300°C.	0.00162 per °C. from 0°C. to 600°C.
Specific gravity....	8.92	8.96	7.73
Specific heat e.g.s. units .....	0.098	0.090	0.115
Melting point .....	1,250° C.	1,180° C.	1,480° C.
Coefficient linear expansion.	20/100°C.-0.0000137	20/200°C.-0.000016	20/100°C.-0.000011 20/500°C.-0.000012
Typical mechanical properties of fully softened material:			
Maximum stress	25/30 tons/sq. in.	20/25 tons/sq. in.	30/37 tons/sq. in.
Elongation .....	51% 90-100	55% 75-85	30/40% 150-180
Brinell hardness			

<sup>a</sup> Whilst this figure may be taken as typical, variations between batches must be expected.

classes of instrument work, but for convenience its properties are listed in Table II.

The search for a suitable alternative to Ferry in thermocouples has also met with no success. The e.m.f. characteristics of Ferry versus copper make it a favourite choice for thermocouples working over moderate temperature ranges, and in the past it has been possible to provide by selection Ferry wire which would give repeatable characteristics over a wide range of temperature. At present the supply of Ferry thermocouple wire is restricted for certain important Government applications, and the only quality of Ferry thermocouple wire now obtainable has e.m.f. characteristics such that the e.m.f. in millivolts against H.C. copper

TABLE II.  
THE PROPERTIES OF TARNAC.

Nominal Composition—	
Nickel .....	4%
Manganese .....	12%
Copper .....	81%
Specific electrical resistance .....	39 microhms/ cm. <sup>3</sup>
Temperature coefficient of resistance.....	0.00001 to 0.00002 per °C.
Melting point .....	1,150° C.
Specific heat .....	0.097
Specific gravity .....	8.39
Tensile strength (soft annealed) .....	25/30 t.s.i.
Coefficient linear expansion .....	0.0000177 per °C.

TABLE III.  
E.M.F. VALUES STANDARD THERMOCOUPLE FERRY v,  
COPPER.

Cold Junction 0° C.		
	Temp. °C.	Millivolts.
	0	0
	20	0.77
	50	2.03
	100	4.24
	150	6.65
	200	9.20
	250	11.90
	.300	14.70
	350	17.65

\* Published by Henry Wiggin and Company Ltd.

† Trade Mark.

is within plus or minus 0·2 millivolts of the figures given in Table III over the temperature range 0° to 350° C.

The Ministry of Supply (Non-Ferrous Metals Control) has decided that it would be unwise to prohibit the use of Ferry altogether, and has directed its attention to defining those uses for which Ferry is still considered essential. The Control has therefore issued an instruction and given a list classifying the uses for which 55-45 copper-nickel alloy is and is not permitted; the latter is reproduced at the end of this article. The instruction in general, permits the use of Ferry for those applications where a very low-temperature coefficient of resistance is essential. In addition, the use of Ferry wire 24 s.w.g. and thinner is permitted, and the use of all gauges of oxidised Ferry wire for close-wound rheostats until a suitable method of producing insulating oxide coatings on alternative materials is found.

TABLE IV.  
RESISTANCE TABLE FOR 12/14 CHROMIUM STAINLESS IRON WIRES.\*

S.w.g.	Diam. in In.	Area in Sq. In.	Ohms ft. at 15° C.	Ohms/ft. at 100° C.	Ohms/ft. at 200° C.	Ohms/ft. at 300° C.
5	0.212	0.0353	0.00748	0.00845	0.00936	0.0109
6	0.192	0.0290	0.00613	0.0103	0.0118	0.0133
7	0.176	0.0243	0.0108	0.0122	0.0139	0.0157
8	0.160	0.0201	0.0131	0.0148	0.0169	0.0190
9	0.144	0.0163	0.0162	0.0183	0.0209	0.0235
10	0.128	0.0129	0.0206	0.0232	0.0266	0.0299
11	0.116	0.0106	0.0251	0.0283	0.0324	0.0365
12	0.104	0.00849	0.0312	0.0352	0.0403	0.0453
13	0.092	0.00665	0.0397	0.0448	0.0512	0.0577
14	0.080	0.00503	0.0525	0.0693	0.0678	0.0763
15	0.072	0.00407	0.0648	0.0732	0.0837	0.0942
16	0.064	0.00322	0.0823	0.0929	0.106	0.119
17	0.056	0.00246	0.107	0.121	0.138	0.155
18	0.048	0.00181	0.146	0.165	0.188	0.212
19	0.040	0.00126	0.210	0.237	0.271	0.305
20	0.036	0.00102	0.260	0.297	0.336	0.378
21	0.032	0.000804	0.329	0.371	0.425	0.478
22	0.028	0.000616	0.429	0.481	0.554	0.623
23	0.024	0.000472	0.583	0.658	0.752	0.847
24	0.022	0.000380	0.696	0.786	0.988	1.01

\* The resistance figures are based on a specific electrical resistance of 66 microhm-cm.<sup>3</sup> for 12/14 chromium stainless iron. Whilst Messrs. Firth, Vickers & Staples Steels Ltd. assure us that this is a typical specific for the material, it is possible that small variations may occur between different batches which will alter the linear resistance.

Ferry is no longer permitted for starters, current controllers, battery charging and plating resistances, arc lamp and welding resistances, and in general for all those resistances where an increase in the resistance of the circuit with temperature rise can either be accommodated or has no fundamental effect on the apparatus. That it is possible to use a material of comparatively high-temperature coefficient for many kinds of control gear and current controllers is shown elsewhere.<sup>1</sup>

A large number of materials, ranging from silicon-copper to stainless steel, have been considered for those applications where Ferry will no longer be permitted, and after considerable investigation we have come to the conclusion that all the requirements of this class of application can be met by two materials with a considerable saving in nickel. These two materials are 80-20 cupro nickel and 12-14 chromium stainless iron. The electrical and other properties of these two alloys are given in Table I, and resistance tables based on these properties follow in Tables IV and V.

The 80-20 cupro-nickel alloy will be suitable for all applications where a moderate temperature coefficient of resistance is required: the 12-14 chromium stainless iron will be satisfactory where a high-temperature coefficient of resistance is of no great consequence.

In substituting 80-20 cupro nickel for Ferry, a further saving in material can usually be effected by reason of the lower specific resistance of the 80-20 cupro nickel.

It is not always possible to reduce the diameter of the 80-20 wire to a point where its lineal resistance is exactly equal to that of the Ferry wire it is designed to replace, as the current carrying capacity of the 80-20 wire may not then be adequate. It is usually possible, however, to reach a compromise in regard to diameter where a longer wire of somewhat less diameter than the original Ferry wire is used and a saving still effected.

In the usual case where Ferry has been employed for a given piece of apparatus the resistance manufacturer should not find much difficulty in calculating the theoretical dimensions of the wire which it is proposed to use as a substitute, whether it be 80-20 cupro nickel or 12-14 chromium stainless iron. The diameter and length of the Ferry wire needed to give the required total resistance and current carrying capacity are known, and the diameter and length in the alternative material needed to give the same characteristics can be ascertained by a simple calculation based on formulae arrived at in the following way.

If two lengths of wire in the two different materials are taken so that their total resistances and superficial areas are respectively equal, then, provided the diameters are not very greatly different, and if we assume their emissivities to be approximately equal, the current carrying capacities of the two wires will be equal under similar operating conditions. Hence, if  $l_1$  = length of Ferry wire and  $D_1$  = diameter of Ferry wire having a total resistance  $R$  ohms, and if  $l_2$  = length of the substitute wire and  $D_2$  = diameter of the substitute wire having a total resistance  $R$  ohms

$$\frac{4 P_1 l_1}{\pi D_1^2} = \frac{4 P_2 l_2}{\pi D_2^2} = R \dots \dots \dots (1)$$

where  $P_1$  = specific resistance of Ferry at the operating temperature, and  $P_2$  = specific resistance of substitute wire at the operating temperature.

If the superficial area of the two wires is the same

$$\pi D_1 l_1 = \pi D_2 l_2 \dots \dots \dots (2)$$

so that  $\frac{l_1}{l_2} = \frac{D_2}{D_1}$

$$\text{and from (1)} \quad \frac{l_1}{l_2} = \frac{P_2}{P_1} \times \frac{D_1^2}{D_2^2}$$

$$\frac{D_2}{D_1} = \frac{P_2}{P_1} \times \frac{D_1^2}{D_2^2}$$

$$\frac{D_2}{D_1} = \sqrt[3]{\frac{P_2}{P_1}}$$

The lengths of the wires are in inverse proportion to their diameters or  $\frac{l_1}{l_2} = \frac{D_2}{D_1}$

A simple calculation will therefore enable the manufacturer to choose a suitable diameter and length of either 80-20 cupro nickel or 12-14 chromium stainless iron wire required to replace Ferry in any given piece of apparatus under the conditions mentioned above.

TABLE VI.

	80/20 Cupro Nickel, $\sqrt[3]{\frac{P_2}{P_1}}$	12/14 Chromium Stainless Iron, $\sqrt[3]{\frac{P_2}{P_1}}$
15° C.	0.818	1.04
100° C.	0.825	1.08
200° C.	0.830	1.13
300° C.	0.835	1.18

To assist in this calculation the factor  $\sqrt{\frac{P_2}{P_1}}$  for 80-20

cupro nickel and for 12-14 chromium stainless iron at 15° C., 100° C., 200° C., and 300° C. has been tabulated in Table VI.

TABLE V.  
RESISTANCE TABLE FOR 80/20 CUPRO-NICKEL GRADE "R" WIRE.

S.w.g.	Diam. in In.	Area in Sq. In.	Ohms/ft. at 15° C.	Ohms/ft. at 100° C.	Ohms/ft. at 200° C.	Ohms/ft. at 300° C.
5	0.212	0.0353	0.00361	0.00368	0.00375	0.00382
6	0.192	0.0290	0.00440	0.00449	0.00458	0.00467
7	0.176	0.0243	0.00524	0.00534	0.00545	0.00556
8	0.160	0.0201	0.00634	0.00647	0.00660	0.00673
9	0.144	0.0163	0.00782	0.00797	0.00812	0.00828
10	0.128	0.0129	0.00991	0.0101	0.0103	0.0105
11	0.116	0.0106	0.0121	0.0123	0.0125	0.0127
12	0.104	0.00849	0.0150	0.0153	0.0156	0.0159
13	0.092	0.00665	0.0192	0.0196	0.0200	0.0204
14	0.080	0.00503	0.0253	0.0258	0.0263	0.0268
15	0.072	0.00407	0.0312	0.0318	0.0324	0.0330
16	0.064	0.00322	0.0397	0.0405	0.0413	0.0421
17	0.056	0.00246	0.0518	0.0528	0.0538	0.0549
18	0.048	0.00181	0.0705	0.0719	0.0733	0.0748
19	0.040	0.00126	0.102	0.104	0.106	0.108
20	0.036	0.00102	0.125	0.128	0.131	0.134
21	0.032	0.0008041	0.158	0.161	0.164	0.167
22	0.028	0.000616	0.207	0.211	0.215	0.219
23	0.024	0.000452	0.281	0.287	0.292	0.298
24	0.022	0.000380	0.335	0.342	0.349	0.356
25	0.020	0.000314	0.406	0.414	0.422	0.430
26	0.018	0.000255	0.501	0.511	0.521	0.531
27	0.0164	0.000211	0.600	0.612	0.624	0.636
28	0.0148	0.000172	0.744	0.759	0.774	0.789

Current carrying tables based on wires which are held horizontally and free to radiate in air, such as are published for Ferry in the Resistance Booklet, issued by Henry Wiggin and Co., Ltd., can only be used as an extremely rough guide to actual practice, since the operating conditions of the wire when wound as a resistance unit are always completely different from those assumed as a basis for the tables. It is always better to choose sizes based on previous practical experience and to calculate the approximate equivalent size of wire required in the substitute material in the way, shown above, or in any other way that the manufacturer may have found suitable, and then to make a practical check on the size chosen by constructing an actual resistance and measuring its characteristics. Nevertheless, for those who require a rough estimate of the current carrying capacity of 80-20 cupro-nickel wires Table VII may be used. This is based on the experimental measurement of the current carrying capacity of wires wound into

TABLE VII.

APPROXIMATE CURRENT CARRYING CAPACITIES FOR 80/20 CUPRO NICKEL.

S.w.g.	Approximate Amps. at Rise of		
	100° C.	200° C.	300° C.
8	34	52	63
9	29	45	55
10	24	38	47
11	20	33	40
12	17	29	36
13	14	23	29
14	11	18	24
15	9	15	21
16	8.3	14	18
17	6.6	11	15
18	5.5	9	12
19	4.6	7.7	10
20	4.0	6.8	9.4
21	3.4	5.9	8.3
22	2.9	5.0	7.2
23	2.3	4.2	6.0
24	2.1	3.8	5.5
25	1.8	3.4	4.9
26	1.6	3.0	4.4
27	1.4	2.7	4.1
28	1.2	2.4	3.5

a small coil on a  $\frac{1}{2}$ -in. diameter mandrel 1 in. long, the gap between turns being equal to the diameter of the wire, and the coil being mounted so as to radiate freely, but protected from draughts.

Similar experimental figures for 12-14 chromium stainless iron are not available, but for wires of equal diameter in two different materials the relative current carrying capacities may be calculated on the assumption that the heat dissipation per unit area of surface of the two wires is the same.

$$\text{Heat input for wire}_1 = \frac{C_1^2 P_1 l_1}{\pi D_1^2} \text{ and surface area of wire}_1 = \pi D_1 l_1.$$

$$\text{Heat input for wire}_2 = \frac{C_2^2 P_2 l_2}{\pi D_2^2} \text{ and surface area of wire}_2 = \pi D_2 l_2.$$

From which

$$\frac{C_1^2 P_1 l_1}{\pi D_1^2 \times \pi D_1 l_1} = \frac{C_2^2 P_2 l_2}{\pi D_2^2 \times \pi D_2 l_2}$$

Since  $D_1 = D_2$

$$C_1^2 P_1 = C_2^2 P_2$$

$$\text{or } C_1 = C_2 \sqrt{\frac{P_2}{P_1}}$$

The current carrying capacities for 12-14 chromium stainless iron wires given in Table VIII have been calculated from those shown for 80-20 cupro nickel in Table VII, using the above relationship.

TABLE VIII.  
APPROXIMATE CURRENT CARRYING CAPACITIES FOR 12/14 CHROMIUM STAINLESS IRON.

S.w.g.	Approximate Amps. at a Rise of		
	100° C.	200° C.	300° C.
8	22	32	37
9	19	28	33
10	16	24	28
11	13	21	24
12	11	18	21
13	9.1	14	17
14	7.2	11	14
15	5.9	9.3	12
16	5.4	8.5	11
17	4.3	7.1	8.9
18	3.6	5.6	7.4
19	3.0	4.8	6.2
20	2.6	4.2	5.5
21	2.2	3.7	4.9
22	1.9	3.1	4.2
23	1.5	2.6	3.5
24	1.4	2.4	3.2
25	1.2	2.1	2.9
26	1.0	1.9	2.6
27	0.91	1.7	2.4
28	0.78	1.5	2.1

It cannot be too strongly emphasised that these figures can only be used as a very rough guide and must always be checked by practical tests. Influences, such as the method of mounting, closeness of spiralling, type and ventilation of case and ambient temperature, have so great an effect on the actual temperature reached by the resistor that the tables may only be used with the greatest of care.

The 80-20 cupro-nickel alloy is, if anything, more ductile than Ferry and can be easily formed into spirals. Its corrosion resistance and resistance to oxidation, though slightly less than that of Ferry, are sufficient for all normal applications. It is available in the form of wire, tape, strip and sheet, but cannot be obtained with an oxide finish which has reliable insulating properties.

Users should specify "Grade 'R' Cupro Nickel" when ordering this alloy for resistance purposes. This will insure that metal specially selected for this particular use will be supplied.

The 12-14 chromium stainless iron, though less ductile than either Ferry or cupro nickel, can be quite easily formed into spirals and most of the forms usually required by rheostat manufacturers. It has good resistance to oxidation at temperatures up to 750°C., with reasonably good corrosion resistance. Henry Wigg n manufacture this alloy only in the form of wire, and tape rolled from wire and supplies in the form of strip or sheet, when required, will have to be obtained from the recognised steel manufacturers. The 12-14 chromium stainless iron wire cannot be supplied with a reliable insulating oxide coating.

It should be realised that the materials referred to in the above discussion have not previously been used to any extent as electrical resistance materials and that, therefore, the electrical properties quoted can only be regarded as typical until more information is accumulated during the course of manufacture. The firm of Henry Wigg n will, however, exercise the same rigid care in the preparation, selection, and drawing of these alloys as they give to Ferry and alloys of the nickel-chromium type. While it may not be possible in the initial stages to meet all the requirements laid down in certain specifications, the Company have no doubt that they will be able to meet normal trade requirements on tolerances. They will be pleased at all times to assist in the selection of alternative materials and in the design of apparatus for which substitute materials have to be used.

## Thickness Testing of Electrodeposits

(Continued from page 94)

### Weighing Methods

These methods essentially consist of a determination of the total weight of deposit on a known area. From the specific gravity of the deposited metal this weight can be converted into total volume of deposit and hence to average thickness over the area under test.

*Difference in Weight.*—This method, which is the one in D.T.D. Specifications 903 and 904, simply consists of weighing a plated article of known area on a sensitive balance, stripping the deposit, reweighing and thereby measuring weight of deposit. Thickness of deposit in metric units is given directly by

$$\frac{\text{Weight}}{\text{Area} \times \text{Spec. gravity}} = \text{thickness.}$$

As, however, weights are usually in grammes, while areas and thicknesses are required in inch units, a simpler formula is

$$\frac{\text{Weight in grammes}}{\text{Area in sq. in.} \times K} = \text{thickness in inches.}$$

$$(K = \text{S.G.} \times 2.54^2)$$

$$\text{S.G.} \times 16.3872.$$

Values for K are: Cadmium, 142; chromium, 116; copper, 146; lead, 186; nickel, 146; silver, 172; tin, 119; zinc, 117.

The specimen under test should be as light in weight and as large in area as possible in order that the weight of deposit should be a weighable proportion of the total weight. For this reason a thin sheet steel test-piece is

NON-FERROUS METALS CONTROL  
PERMITTED AND PROHIBITED USES OF 55/45 TYPE COPPER-NICKEL ALLOYS AS RESISTANCE MATERIAL  
(These Classes do not refer to wire 24 s.w.g. and thinner.)

CLASS A.	CLASS B.
Alloy should not be used for the following unless there are exceptional features of which full technical details must be given.	Alloy permitted provided its use is justified for technical reasons. Alternative should be employed if possible.
1. Starters for all kinds of electric motors.	1. <sup>1</sup> Slide wire rheostats depending on an oxide coating on the wire for insulation between turns.
2. Resistances for reverse current and dynamic braking.	2. Thermal overloads.
3. Speed regulators with the exception of those permitted in Class B, Items 3 and 4.	3. Ward Leonard control of machine tools, but not for the starter or speed regulator of the motor of the M.G. set.
4. Series resistances for arc lamps and welding equipment.	4. Shunt speed regulators for d.c. motors when used with machine tools.
5. Current controllers and regulators of all kinds, including battery charging and plating, except Class B, Item 1.	5. Swamping or ballast resistances used to eliminate the effect of temperature change, but not cases such as instruments where manganese type alloy can be employed. Also including swamping resistances for contactor coils.
6. Ballast resistances for measuring instruments.	6. Thermocouple wires.
7. Contactor shading ring series resistances.	7. High-resistance risers for rotary converters, variable voltage generators and a.c. commutator motors.
8. Resistance units employed in various types of instruments and light current equipment, e.g., radio sets.	8. As replacement of damaged equipment where the same material was previously employed.
9. Heating units of all kinds, with the exception of Item 2, Class B.	9. <sup>2</sup> Ammeter shunts.

<sup>1</sup> No alternatives at present available.

<sup>2</sup> Attention is drawn to the fact that on technical grounds manganese type alloys provide a satisfactory alternative for this use, and it may be necessary at a later date to transfer ammeter shunts to Class A.

Unless special conditions obtain, no non-ferrous materials will be released for items 1, 2, 4 and 5 in Class A.

advisable. This is plated at the same time as the batch of work under test, taking care that its position in the vat is such as to produce a fair and representative sample of the deposit that is being applied to the bulk load.

The specimen must be carefully cleaned and dried before weighing, and the procedure adopted must be faithfully followed when cleaning and drying preparatory to the second weighing. The stripping process in use must remove every trace of deposit, but must not attack the basis metal. When this cannot be achieved the weight of deposit must be determined chemically.

*Chemical Determination.*—The deposit is dissolved completely in a suitable reagent, the stripped specimen removed and rinsed into the solution, and the dissolved plating estimated by chemical analysis. Provided the basis metal does not contain any element similar to the metal of the deposit, the accuracy of this method is not affected by partial solution of the basis metal.

*Larkin's Method.*—Unlike the two previous methods, this new procedure, described by Larkin,<sup>†</sup> does not require the deposit to be stripped from the basis metal. The principle of the method depends upon the fact that the density of the deposit is different from that of the basis metal, thus a plated article will have a resultant density either greater or less than that of the unplated article. As the specific gravity of iron (or steel) does not clash with that of the plated metals, it is probably safe to assume that all deposits upon iron or steel can be measured in this way.

